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THE

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

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THE CHEMICAL NEWS.

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No. 2249.—JANUARY 2, 1903.

THE DIRECT CONVERSION OF CHARCOAL INTO DIAMOND.

The Converse of Pepys' Experiment.

By Dr. ALBERT LUDWIG.

One of the most essential relations between electrical and radiant energy is expressed by a law of nature, according to which all transparent elementary bodies are non-conductors of electricity. I employed conformity to this law as a criterion of the possibility of converting carbon into its different forms. Thus, if by any process whatever charcoal is converted into diamond, this change must be recognised by the resulting non-conductivity of the carbon, which could be easily proved by suitable instruments. Further, I started from the assumption that in almost all cases an allotropic change may be effected by simple alteration of temperature, at ordinary or increased pressure. There is no instance in which, apart from chemical influences, any desired form of such an element cannot be obtained by raising or lowering the temperature. In all cases in which other bodies are favourable to the reaction, what actually occurs is only a lowering of the temperature of conversion. Thus, in the preparation of red phosphorus, iodine effects the change at a far lower temperature. In the present case, at a red heat iron enters into combination with carbon as diamond, and Pepys showed this by the change of a glowing iron wire brought into contact with diamond into steel. If it is required to change carbon directly into graphite, as is known, a very much higher temperature is needed. I was able to show that in all these reactions under strong gaseous pressure (pressures up to 3100 atmospheres were used) the formation of diamond results either at a lower temperature in presence of iron (red heat) or at the melting-point of carbon without using such a contact agent. An iron spiral was embedded in retort carbon powder, and heated to a red heat by an electric current in an atmosphere of hydrogen at high pressure. A few minutes after the current began to pass, the low resistance originally caused by the conducting carbon rose to the value of the resistance of the iron spiral. The charcoal in contact with the spiral had thus become a non-conductor. Careful examination showed on some of the little pieces of carbon bright glittering crystals with the specific properties (hardness, specific gravity, refraction) of diamond. A great part of the carbon present in the iron spiral was likewise changed into diamond. The characteristic appearance of these little crystals was worthy of remark; the strongly marked pitting of their surfaces calling to mind Moissan's diamonds. Undoubtedly, here the iron brought about the reaction which ensued at so low a temperature. If it is required to convert charcoal into diamond without the presence of iron, numerous experiments showed that it is necessary to melt the carbon in an atmosphere at very high pressure. In fact, it was successfully proved that molten carbon is non-conducting, and is thus diamond. At the gaseous pressures used in this case the carbon melts very easily by the help of a metallic arc lamp, and was thus obtained in small spheres, about the size of a pea, of great hardness, and having the crystalline structure of naturally occurring carbonados.

This reaction might obviously be used to prepare diamonds on a large scale, even to enter into competition with natural diamonds, if certain conditions must be maintained; these are easily fulfilled if sufficient means are at hand, and I shall return to this subject at the proper time.

I will here describe one more experiment which explains the non-existence in nature of silicon carbides. Powdered carbon was mixed with different silicates, and exposed for about fifteen minutes to the action of a strong arc (under strong pressure) generated by means of a 5 horse-power machine. A research performed by Fresenius, in Wiesbaden, showed that all the carbon was present in the free state. Thus the proof could be deduced that at the high gas pressures occurring at a temperature at which carbon is melted no carbide could be formed. An explanation of this peculiar behaviour of carbon ought not to be difficult to find (Gibbs and Helmholtz, "Law of Entropy").—*Chemiker Zeitung*, 1902, xxv., 89.

ON CERTAIN PROPERTIES OF THE ALLOYS OF THE GOLD-SILVER SERIES.*

By the late Sir W. C. ROBERTS-AUSTEN, K.C.B., D.C.L., F.R.S., and T. KIRKE ROSE, D.Sc.

In a former communication to the Society (*Roy. Soc. Proc.*, 1900, vol. lxvii., p. 105) the curve of the initial freezing-points of the alloys of gold and copper and some micrographic evidence as to their structure were given, and it was shown that, according to the theory of solutions, the alloys rich in gold should not be homogenous after they have solidified. The fact that they are not uniform was confirmed by analysis. The subject has, however, more than theoretical interest, and the inference was drawn that standard gold, which consists of eleven parts by weight of gold to one of copper, is unsuitable as a material for the preparation of the trial plates by which

* A Paper read before the Royal Society, December 11, 1902.

the standard of the coinage is tested. These trial plates according to law must contain 916·6 parts of gold and 83·3 of "alloy," that is of some other metal, and it remained to be determined what the other metal should be.

It will be at once apparent that the alloy or mixture of the two metals must, if the cold mass is to be uniform, solidify as a whole; that is to say, that the crystals first formed should be of the same composition as the mother-liquor, and this condition can be fulfilled by isomorphous mixtures only. It has long been recognised that the gold-silver alloys are cases of isomorphism, and Gautier, in 1896, stated (*Bull. de la Soc. d'Encouragement*, October, 1896) that the freezing-point curve of the series followed a straight line if the percentages by weight of the constituents were taken as abscissæ.

This curve was re-determined by experiment, a number of alloys being made up and autographic records taken of their cooling curves by the Roberts-Austen recording pyrometer. The results obtained are given in the following table. The freezing-point of gold was taken as 1064°.

Percentage of gold present in alloy.		
By weight.	In atoms.	Freezing-point.
100	100	1064°
80·99	70·25	1061
64·60	49·97	1061
54·80	39·89	1046
43·98	30·07	1044
31·71	20·28	1028
17·23	10·23	1001

The following points have been observed by Heycock and Neville (*Phil. Trans.*, A, 1897, vol. clxxxix., p. 69):—

2·26	1·25	962°
0·91	0·50	961
0	0	960

It will be seen that Gautier's conclusion is substantially confirmed, but it was observed, as one of us had previously pointed out (Roberts-Austen, *Proc. Inst. Mechanical Engineers*, 1891, p. 564), that the first additions of silver did not depress the freezing-point of gold. So far does this property extend that even the alloy containing 50 atoms of gold to 50 of silver, or 64·6 per cent of gold by weight, solidifies at 1061°, which is only 3° below the freezing-point of pure gold. With further additions of silver there is a steady acceleration in the rate of lowering of the point of solidification, so that the freezing-point curve of the series has no double flexure, unless one is indicated near the silver end of the curve by Heycock and Neville's results.

There is, of course, no eutectic alloy observable in any member of the series.

The alloys all consist of large grains, but these are built up of smaller grains, so that the ultimate structure is exceedingly minute. When magnified 1500 diameters the grains appear as small irregular crystals of the cubic system. In order to develop any segregation that might take place, an ingot of the standard alloy containing 91·66 per cent of gold by weight was heated for two months in one of the annealing furnaces at the Royal Mint, the temperature of which was kept at about 700° by day, but fell to about 100° at night. The maximum temperature attained was over 300° below the fusing-point of the alloy, and the sharpness of the angles of the specimen had suffered no change. After this treatment it was found that the grains had increased in size, and the crystals forming them had become well developed. No true segregation, however, could be detected even in this ingot, either by analysis or by the microscope, and plates prepared by rolling out ingots containing 916·6 parts by weight of gold, and 83·3 parts of silver, were found on analysis to be uniform in composition.

The ancient trial plates, according to the analysis made by one of us (Roberts-Austen, *Chem. Soc. Journ.*, 1874, p. 197), consist of a triple alloy of gold, silver, and copper. The earliest one in existence was made in 1527, the year following the first introduction of the standard 916·6. This plate contained only 0·62 per cent of copper, and was probably intended to consist of gold and silver only. All subsequent plates, however, down to that made in 1829, contained much larger amounts of copper. In 1873 it was determined to omit the silver and to use only copper as the alloying metal, and thus to preserve identity of composition between the trial plate made in that year and the coinage. In view, however, of the importance of obtaining homogeneous trial plates and of the ease with which the exact quantity of copper required to make the assay pieces identical in composition can be added to the pieces of the trial plate during the course of the assays, it is preferable to use only silver as the alloying metal in the manufacture of the trial plates.

Such an alloy has accordingly been used at the Royal Mint since the beginning of the present year instead of fine gold for checks in the assay of standard bars and coins. In view of the minute accuracy with which the operations of coinage have to be conducted, this is a matter of much importance. By this method any errors are avoided which might be caused by accidental variations in weights occurring after the trial plates have been made.

ABNORMAL CHANGES IN SOME LINES IN THE SPECTRUM OF LITHIUM.*

By HUGH RAMAGE, B.A., St. John's College, Cambridge.

In the course of an investigation on the flame spectra of metals, the writer has examined the spectrum of lithium. Some facts have been discovered of sufficient importance for a separate paper.

The same spectrometer was used as in the investigation on the "Spectra of Potassium, &c." (*Roy. Soc. Proc.*, 1902, vol. lxx., p. 303). Whilst the wave-lengths of some of the lines in the flame spectrum of lithium agree closely with those given by Kayser and Runge for the lines in the arc spectrum (*Berlin Akad. Abhandl.*, 1890, vol. iv., p. 19), the wave-lengths of other lines differ considerably from these. The numbers and differences are given in the accompanying table.

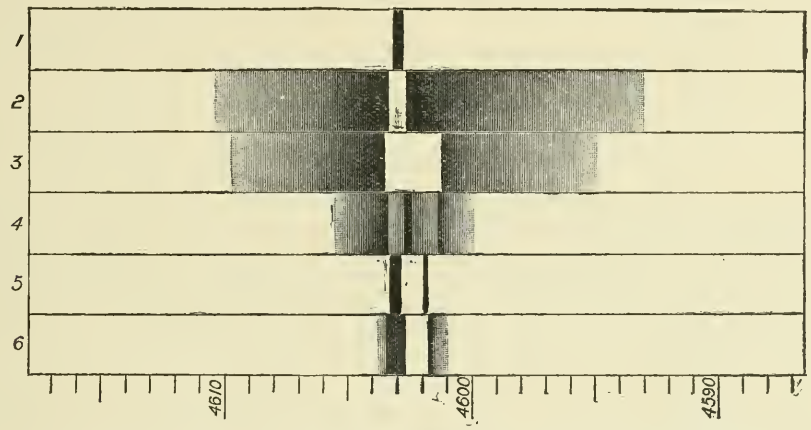
The only important differences occur in the lines of the first subordinate series. Exner and Haschek have given the wave-lengths of three lines in the spark spectrum (*Sitzber. Kais. Akad. Wien.*, 1897, vol. cvi., Abth. 2A, p. 1133) as 2815·55, 3232·91, and 4603·10. The last is described as reversed. Eder and Valenta have given the wave-length of the blue line in the Bunsen flame spectrum as 4602·4 (*Denkschr. Kais. Akad. Wien.*, 1893, vol. lx), and as 4602·46 in the spark spectrum when a condenser was used (*Denkschr. Kais. Akad. Wien.*, 1898, vol. lxvii.). They described the latter measurement as that of the middle of a broad dark line, the less refrangible wing of which was stronger than the other, and diffuse towards the red. They also gave measurements of five other lines, and these agree closely with the arc lines given by Kayser and Runge. Professor Hartley recorded four lines in the oxyhydrogen flame spectrum of lithium chloride (*Phil. Trans.*, A., 1894, vol. clxxxv., p. 177) corresponding to the first, fourth, sixth, and eleventh of the lines in the above table. The blue line was measured in the flame spectrum on four plates, and the results differed only in the second decimal place, the figures in which were 8, 7, 6, and 7. Professors Liveing and Dewar made some observations by eye on the appearance of the blue line in the arc spectrum which led them to believe there were two lines, a strong one with a weak line on the more refrangible side (*Phil. Trans.*, 1883, vol. clxxiv., p. 215), and Kayser and Runge, after referring to this, say (*Ibid.*, p. 20):—"Wir

* A Paper read before the Royal Society, December 11, 1902.

Oxyhydrogen flame spectrum (Author).		Arc spectrum (Kayser and Runge).					
		Principal series.		Second subordinate series.		First subordinate series.	
Wave-length.	Intensity.	Wave-length.	Difference from flame.	Wave-length.	Difference from flame.	Wave-length.	Difference from flame.
6708	10	6708·2	—				
6103·84	9					6103·77	−0·07
4971·98	2			4972·11	+0·13		
4603·07	7					4602·37	−0·70
4273·34	1			4273·44	+0·10		
4132·93	5					4132·44	−0·49
3985·86	<1			3985·94	+0·08		
3915·59	3					3915·2	−0·39
3795·18	2					3794·9	−0·28
3719	1					3718·9	—
3232·82	4	3232·77	−0·05				
2741·43	1	2741·39	−0·04				

The flame lines are all sharp.

Kayser and Runge describe the lines 6708·2, 3232·77, 2741·39, and 6103·77 as "mostly reversed"; the lines in the second subordinate series as diffuse towards the red; the lines 4602·37 and 4132·44 as reversed; and the latter, with the remaining lines in the same series, as diffuse on both sides.



DIAGRAMS OF THE BLUE LITHIUM LINE AS IT APPEARS IN PHOTOGRAPHS.

The fine vertical lines are merely shading lines; the broad wings of the actual lines in the spectra are continuous.

1. Bright line of flame, arc and spark spectra.
2. Reversed line from dense outer flame of arc.
3. Reversed line from inner cone of strong arcs and from near negative pole of weak arcs.
4. Broad line with two absorption bands, from arc spectrum.

5 and 6. From spectrum of thin outer flame of arc with different exposures.

haben nur bei zwei Aufnahmen neben der Hauptlinie eine zweite schwache umgekehrte Linie bein 4603·13 erhalten; da aber hier eine Eisenlinie liegt, glaeben wir, dass dies eben die Eisenlinie ist, welche sich durch den hellen Hintergrund der Lithiumlinie umgekehrt hat."

The wave-length of the line which Kayser and Runge attributed to iron agrees with that obtained by the author for the bright line in the flame spectrum, and by Exner and Haschek for the reversed line in a spark spectrum. It was decided in view of these differences to take a series of photographs of the arc spectrum of lithium, using the carbonate of lithium on carbon poles, and to study especially the appearances of the blue line. The results will now be briefly described.

A Gulcher arc lamp with vertical carbons was used. When the arc was started with a quantity of lithium carbonate on the carbons, a large proportion of the salt was freely volatilised and expelled in the form of a dense vapour. As the arc lamp was placed, the magnetic field produced by the feed mechanism caused the bulk of the vapour to be expelled in the direction of the collimator. Photographs of the spectrum taken at this early stage show the line as a very broad bright line extending from 4610·4 to 4593·5, with a narrow dark line extending (2 in figure) from 4603·46 to 4602·71, having its middle (measured) at 4603·06. The middle of the broad bright line is, according to the above, at wave length 4601·95, and the middle of the dark line (reversed) is coincident with the bright line of the flame spectrum.

One pole of a weak bar magnet was placed near the arc so as to direct the expelled vapour in a direction perpendicular to the axis of the collimator. After the large excess of the lithium salt had been volatilised, the image of the central portion of the arc was thrown on the slit, and the spectrum photographed, when the ends of the carbon poles, not widely separated, were red-hot. The lithium vapour in the central core was doubtless at a very high temperature, and there was only a thin layer of cooler vapour between it and the slit. Under these conditions the bright line is again broadly expanded, and so also is the dark line, for it now extends from 4603·55 to 4601·25 (mean = 4602·40) on one photograph (3 in figure), and from 4603·68 to 4601·22 (mean = 4602·45) on another. The bright wings are nearly of the same intensity and extent. The middles of these two dark lines are nearly the same as the wave-length 4602·37, given by Kayser and Runge, and by Eder and Valenta for the reversed lines.

Some photographs were also taken of the spectrum of the transparent flame which issued from the arc, the bar magnet being used as above. With a short exposure one

narrow bright line was obtained of wave-length 4603·06; with a longer exposure this bright line was much stronger, and there was the appearance of a weak line on its more refrangible side, exactly as Professors Liveing and Dewar described. The wave-lengths of these two were 4603·18 and 4601·89 respectively on one photograph (5 in figure), and 4603·12 and 4601·65 on another, The last line was fairly sharp on the less refrangible side, whilst it faded gradually on the other side (6 in figure). With still longer exposures the weaker line could not be distinguished from the wing of the much expanded bright line. This wing when weak always resembles a line, and it was thought that a line might be nearly coincident with its less refrangible edge. Measurements showed that this edge varied in position on different photographs, but Professor Liveing suggested that the tip might be formed by a line, and if so, the tip should always have the same wave-length. The following table gives the wave-lengths of the two tips on different photographs:—

Spectrum.	Tip of weaker side.	Tip of stronger side.
206^3	4601·68	
213^4	·83	4603·11
213^6	·66	·11
214^1	·72	·03
222^6	·78	·10
222^7	·82	·11
224^6	·82	
226^5	·83	
226^7	·95	4603·21
232^6	·79	

This evidence is not conclusive; both tips appear to vary, but the weaker one varies more than the other. The arc, in these experiments, was formed with a Gulcher lamp with the carbons vertical, the positive being uppermost, and the image of the arc projected on to the slit of the collimator by a lens. It was observed that the less refrangible point, wave-length 4603·1, was, in many photographs, higher on the plate than the weaker point; it was given out by vapour quite near to the positive pole. It was observed also in some photographs that the line extending from it faded away lower down; the vapour near the negative pole did not emit this line, but gave the broad bright line with the broad dark line down its middle. This broad bright line fades away as the positive pole is approached; the more refrangible wing ends in a point, but the less refrangible wing is lost in the bright line of wave-length 4603·1. There appears then in the middle portion of the spectrum a broad dark line with wings of unequal extent, and the less refrangible wing is broader, and, near its more refrangible edge, much stronger than the other wing. The broad dark line extended on such photographs from (1) 4602·72 to 4601 81, (2) 4602·86 to 4602·05, (3) 4602·73 to 4601·62, and in two other cases, where there were less differences of intensity between the two wings, from 4603·26 to 4601·61 and from 4603·07 to 4601·59. There were indications on some photographs of a bright line near the middle of the broad dark line; the measurements of such a photograph gave:—

Less refrangible edge of broad dark line ..	4603·40
Apparent bright line	4602·57
More refrangible edge of broad dark line ..	4601·31

The absorption bands of reversals in such a photograph as this are comparatively bright, for there is considerable action on the plate where the images of these bands fall (4 in figure). The effect is probably due to the superposition of the spectrum of the outer flame upon that of the inner core when both are giving reversed lines.

Some observations were made at Professor Liveing's suggestion on the arc spectrum of lithium when the arc was formed between carbon electrodes inserted horizontally in a magnesia brick. The arc enclosed in this way is much steadier than in the open. The light which was examined passed out through a horizontal hole perpendicular to the carbons. The differences described above between the spectra of the vapours near the two poles were easily observed by eye observations.

Photographs of the spark spectra of lithium were taken in the hope of finding a second line which would account for the remarkable differences in the arc spectra, but no second line was found. A piece of metallic lithium was placed in a cup formed in the end of an aluminium rod, and sparks were passed between this and an aluminium wire held immediately over the lithium. No Leyden-jar was put into the secondary circuit at first, and it was found that photographs of the blue line were obtained with exposures of fifteen minutes. The lines were sharp, and showed no signs of reversal. The wave-length of the blue line was found to be 4603·08. The vapour near the electrodes gave broader lines than the vapour a short distance away. The broadening was much greater at the negative electrode than the positive, and it extended further on the more refrangible side than on the other side. The bright line and the broad reversed line were, in fact, both present in the spectrum of the spark, near the negative electrode.

It was much more difficult to obtain photographs of the spark spectrum when a Leyden-jar was introduced. Some were obtained from moist lithium carbonate which had been fused into the aluminium cup. The blue line was very weak and nebulous, and it was difficult to obtain measurements of it. The following were obtained from four photographs:—4603·18, 4603·14, 4602·99, and 4603·97; the mean of these is 4603·15. Better photographs were obtained when a coil of wire was also introduced into the secondary circuit. The line more nearly resembled that obtained when no Leyden-jar was used; the broad reversed line was more clearly defined at the electrode when negative than when positive.

An attempt was made to photograph the blue line in the Bunsen flame spectrum, but with an exposure of six hours no trace of it was obtained.

Other Lines in the Spectrum of Lithium.

The orange line was examined in the arc and flame spectra by eye observations and by photography. The line in the flame spectrum was measured on four plates:—

Spectrum.	Wave-length.
244^2	6103·84 centre of line.
244^2	6103·85 near tip of line.
244^4	6103·88 rather strong line.
245^2	6103·84
245^3	6103·83

The mean of these, omitting the rather strong line, is 6103·84. None of these lines showed any signs of reversal.

The wave-length of the bright line in the arc produced by the Gulcher lamp in the open was:—

Spectrum.	Wave-length.
241^6	6103·81 nebulous in middle with sharp points. The nebulous part extended from 6102·46 to 6104·94.
242^4	6103·86
242^5	6103·82

The mean result is 6103·83

The orange line is easily reversed in the arc. The reversed line was photographed and the wave-length measured on two plates, the results being 6103·82 and 6103·84. The reversal was narrow and the wings did not extend very far. The more refrangible wing was slightly broader than the other, and this difference was observed in the photographs and by eye observations. The part of the arc near the negative pole was examined very carefully; the line was most sharply reversed in that part, but there was no trace of a broad dark line. The orange line, with the exceptions noted, behaved normally

Measurements were also made of the two other lines in the arc spectrum. The wave-length of a weak and very diffuse line on one plate was 4132·82, and that of a very weak sharp line 4273·32. The former line on another plate was stronger and broader; its middle was at 4132·35, whilst the other line, much broadened towards the red, had its strongest part at 4273·62.

The current used in working both the open and enclosed arcs was about 9 ampères. Kayser and Runge employed a current of 25—35 ampères from one machine, and, to bring out the weak lines in some spectra, a current of 40—50 ampères from another machine. It seems probable that they worked with the intense arc which was only obtained by the author when the carbons were very near together, and that they observed only the spectrum of broadened lines which the author found was emitted by the intense arc and near the negative pole by weaker arcs. Their remarks on the appearances of the lines in the first and second subordinate series confirm this view. Eder and Valenta obtained a similar spectrum to Kayser and Runge's arc spectrum in the spark spectrum of metallic lithium when they used a condenser in the secondary circuit.

The author has pleasure in thanking Professor Liveing for the interest he has taken in this work and for some useful suggestions.

Conclusions.

The lines in the principal series of lithium appear to broaden and reverse normally.

The lines in the second subordinate series do not reverse even in the arc, but in strong arcs they broaden towards the less refrangible end of the spectrum and become diffuse on that side.

The first line in the first subordinate series, wave-length 6103·84, is almost normal; it broadens slightly more on the more refrangible side than on the other. The other lines in this series also broaden on both sides and become diffuse, but they broaden more rapidly on the more refrangible side than on the other. The centres of the broadened lines are more refrangible than the corresponding lines in the narrow state. The inner core of intense arcs, and the parts near the negative poles of weak arcs and sparks, give a broad reversed line with its centre about wave-length 4602·4; whilst the part near the positive pole in weak arcs, and the flame of the arc, give a sharp bright line, wave-length 4603·07, coincident with the lines in the spectra of the oxyhydrogen flame and uncondensed spark. The similar changes in the other lines diminish with their refrangibility. The wave-lengths hitherto recorded for these diffuse lithium lines would appear to be those of abnormal lines. The true lines are the sharp bright ones which occur, without complication, in the spectrum of lithium in the oxyhydrogen flame.

(Added Nov. 28, 1902.—Since this paper was communicated to the Royal Society, I have seen a paper on the spectrum of lithium, by Hagenbach, in the *Annalen der Physik*, No. 12, 1902, which was published on November 13. His conclusion that there are two lines near wave-length 4603 is not, I think, established; and I still hold that the views expressed in this paper are more probable. He has not been able to find the second line as a bright line, so the difficulties in the way of accepting the view that there is a second dark line, without a corresponding bright line, remain. He has nor referred to Professors Liveing and Dewar's work (*Phil. Trans.*, 1883, vol. clxxiv., p. 215), and his evidence for saying there are two lines is, in fact, similar to the evidence they gave.)

Dichlorhydrate and Dibromhydrate of Cadinene.—Emilien Grimal.—The author succeeds in isolating the *d*-dichlorhydrate of *d*-cadinene, the *d*-dibromhydrate of *d*-cadinene, and a new *d*-cadinene, quite unknown before. —*Comptes Rendus*, cxxxv., No. 23.

NOTES ON THE ICELAND SPAR METHOD FOR THE STANDARDISATION OF HYDROCHLORIC ACID.

By W. HEBER GREEN, M.Sc.

In this method as proposed by Professor Masson (Chem. News, 1900, vol. lxxxi., p. 73), a dry beaker containing 2½—3½ grms. of Iceland spar is accurately weighed, and exactly 20 c.c. of the approximately normal hydrochloric acid are run in from a burette, the point of the burette and a watch-glass covering the beaker, being so arranged as to prevent loss from spirting.

After at least three or four hours, the covered beaker is raised to the boiling-point, and kept at or about that temperature for one hour. This drives off carbonic acid, and ensures the completion of the action.

The perfectly clear and neutral calcium chloride solution is now decanted off, and the beaker and residual spar (still in compact lumps) are thoroughly washed, dried at 110° C., cooled, and weighed.

The molecular weight of $CaCO_3$ being taken as 100·0 it follows that the difference between the original and final weighings (in grms.) will give without further calculation the "factor" of the hydrochloric acid.

For the last three years this method has been in constant use here in Melbourne, and it has been found that students inexperienced in quantitative work obtain results with this process involving errors of about 1 per cent in their first attempts, but hardly more than 1 in 1000 after they have had some practice.

Among the sources of error mentioned by Professor Masson the following seem to be of possible importance:—

1. The measurement of the acid.
2. Loss of weight of the beaker, due to solution of the glass during neutralisation.
3. The atomic weight of calcium is taken as 40·00, whereas the recent work by Hinrichsen gives 40·14. This introduces an uncertainty of over 1 in 1000.

The Measurement of the Acid.

With due attention to temperature and burette calibration and cleanliness, the accuracy obtained should be at least as great as in any volumetric work.

The use of a standard pipette instead of a burette was suggested as being possibly more accurate.

A number of experiments showed that when cleansed from grease by alkali the average divergence from the mean amounted to about 0·003 c.c. with a 20 c.c. pipette, but if allowed to become greasy again by several days' use or even exposure to the air without re-cleansing, discrepancies of 0·015 c.c. may be expected. With a carefully cleansed burette (an alcoholic solution of soap is recommended for this purpose) volumes agreeing to within 0·01 c.c. may be measured.

Loss of Weight of the Beaker.

The researches of Pfeiffer, Mylius, and Foerster, Weber and Sauer, and Kohlrausch (*vide Ber.*, 1892, xxv.) show that glass, consisting as it does mainly of sodium or potassium and calcium silicates, when acted on by water, loses some of its alkali, which (if not neutralised by the presence of acid) exerts its own influence in dissolving silica as well.

Consequently, acids dissolve less than pure water, whilst alkalis attack the glass as a whole, and in this respect are similar to hot and especially superheated water, which is also a solvent for silica itself.

The action of salts depends on the concentration and on the reactions which take place between them and the substances extracted from the glass.

Hot water dissolves glass much more rapidly than cold water, and considerably diminishes its solubility in the latter (Pfeiffer, *Ann. Phys. Chem.*, [2], xliv., 239),

TABLE I.

No.	Description.	Weight.	Total area of surface.	Previous loss.	Loss when boiled in 4E-HCl for two hours.	Total loss per sq. decimetre.
		Grms.	Sq. c.m.	M.grms.	M grms.	M.grms.
I.	7-oz. Bohemian glass beakers	24·6	330	3·8	2·9	2·03
II.		27·7	330	4·8	1·8	2·00
III.	5-oz. Bohemian glass beakers	19·8	220	Unused	2·6	1·18
IV.		15·8	220	Unused	2·55	1·16

TABLE II.

	Description of vessels.	Weight.	Total area of surface.	Loss on boiling for two hours in 4E-HCl.	Loss during first standardisation.	Loss on boiling for two hours in 2E-$CaCl_2$ and two hours in water.	Loss after one week in water at 25° C.	Loss during second standardisation.	Total loss per square decimetre.
		Grms.	Sq. cm.	M.grms.	M.grms.	M.grms.	M.grms.	M.grms.	M.grms.
V.	5-oz. Bohemian glass beakers	18·2	220	7·4	0·65	1·85	0·0	0·55	4·75
VI.		20·8	220	4·25 (*a*)	0·45	2·05	0·05	0·3	3·25 (*a*)
VII.	5-oz. conical parting flasks	32·7	290	(6·4?)	1·55	2·45	—	—	3·58
VIII.		32·4	290	6·35	1·4	(2·4?)	0·0	—	3·50
IX.	50 c.c. Jena glass flasks	23·0	240	0·85	0·35	−0·1	—	0·1	0·55
X.		19·8	240	0·9	0·45	+0·05	—	0·1	0·65

(*a*) Beaker VI. had been previously used for analytical work.

The best glass for chemical purposes has a composition approximating to the formula—

$$3(K_2O(\text{or } Na_2O).3SiO_2).2(CaO.3SiO_2).$$

In the Iceland spar method the glass beaker is exposed to the action of a cold acid solution of calcium chloride for a period which may vary from three or four hours to over twenty hours, and to a boiling solution of calcium chloride, which rapidly becomes neutral, for one hour.

Any alkali dissolved out of the glass in the cold, or before all the hydrochloric acid has been neutralised, will cause some of this acid to be converted into sodium or potassium chloride instead of dissolving its equivalent quantity of spar. Any solution of the glass after that time, however, will not affect the amount of spar dissolved, but will necessitate the taring of the empty beaker before and after the experiment.

The total amount dissolved has hitherto been assumed to be negligible, but discordant results obtained by students in the University laboratory, especially when new beakers have been used, have given rise to the suspicion that an appreciable error may be so introduced.

One student was asked to weigh the beakers (previously unused) before and after each experiment.

The losses he observed were :—

	Beaker I.	Beaker II.
	M.grms.	M.grms.
During first standardisation ..	2·1	2·5
During second standardisation ..	1·3	1·2
During third standardisation ..	0 4	1·1
Total loss of weight	3·8	4·8

But his results were not concordant enough to indicate how much, if any, of the hydrochloric acid had been neutralised by the alkali dissolved from the glass. Taking advantage of the necessity which arose (in connection with other research work) of standardising with accuracy an approximately normal hydrochloric acid solution, it was decided to investigate this source of error more thoroughly.

The two beakers above mentioned and two new ones (for comparison) were placed in a large beaker together, and were covered with 4E-HCl (*vide* Reddrop's system, CHEMICAL NEWS, 1890, vol. lxi.), which was kept at the boil for two hours. (See Table I.).

Evidently the previous loss of I. and II. has only diminished their solubility, neither can III. and IV. be considered as having been rendered completely insoluble, but it seems probable that little further loss would take place in a calc-spar experiment before all the acid had been neutralised, and, consequently, the loss in weight of the glass, if any, subtracted from the apparent loss of spar should give the true strength of acid.

As this make of beakers (recently imported from an English firm) showed a tendency to devitrify if overheated in the air-bath, they were discarded and other vessels employed.

After weighing, the six beakers and flasks used were rinsed in hot dilute alkali to cleanse them from grease, and were then boiled in 4E-HCl for about two hours; they were washed with distilled water, dried, and weighed.

In each beaker or flask were placed 2—3 grms. of Iceland spar (in two or three lumps which had been previously treated with dilute acid to round the corners), and the vessels were re-weighed.

The standard acid was measured with a 20 c.c. pipette; the temperature being noted. The importance of this precaution does not seem to be sufficiently recognised. (An alteration of 4° C. will affect the normality to the extent of 1 in 1000).

The beakers were covered with suitable watch-glasses, which were moved slightly to one side to allow the point of the pipette to be introduced; in the case of the flasks the acid was run through a small funnel placed in the neck to avoid loss by spirting of the acid, and the funnel was then rinsed with water.

The vessels were left to stand over night, and next day raised to the boiling-point on a clean asbestos card, and kept at—or about—that temperature for one and a half to two hours. This time was unnecessarily long, one hour at the boiling-point sufficing to neutralise any acid that may remain after standing over twelve hours in the cold, and to remove dissolved carbonic acid. Neutralisation may be taken as complete when bubbles of carbonic acid are no longer given off, and the liquid shows a tendency to bump.

The calcium chloride solution was decanted off, and kept, in each case with its own washings, in separate vessels.

The beakers and residual spar were dried, cooled, and weighed as described in Professor Masson's paper. Finally, the spar was emptied out, and the vessels themselves re-weighed. (See Table II.).

In order to test the effect of calcium chloride on the glass, 25 c.c. of 2E-$CaCl_2$ (neutral to litmus) was placed in each vessel and boiled for two hours, and then the solution was rinsed out and replaced by a similar amount of water which was also boiled for two hours. In the case of the Jena flasks, the calcium chloride solution was accidentally boiled down to 4 or 5 c.c., and some difficulty was found in washing the flask out, possibly accounting for the slight gain observed in IX.

Beakers V. and VI. and Flask VIII. were immersed in

a water-bath kept at 25° C. for a week, and in only one case was any loss perceptible on a balance capable of weighing accurately to 0·05 m.grm.

This confirms Pfeiffer's conclusion that treatment with hot water protects the glass from further action of water at a lower temperature.

Attention is directed to the behaviour of the Bohemian glass beakers and the Jena glass flasks when employed in a second standardisation after the experiments described above.

The Jena glass is seen to be far superior, and I would suggest that *for the Iceland spar method, conical Jena glass flasks (Erlenmeyer pattern) be employed after having been boiled for* three to four *hours with acidulated water*, a treatment which should be applied to all pycnometers, Sprengel tubes, and other glass vessels which are supposed to remain constant in weight although exposed to the action of water or aqueous solutions.

The results given in Table III. clearly justify the assumption that the glass vessels employed in the standardisation, when treated as directed, did not appreciably lose weight until all the acid had been neutralised; for the maximum variation from the mean value (0·99803), found as the normality of the acid, is not more than 0·00013—a quantity within the error of the pipette measurement.

The Molecular Weight of the Iceland Spar Employed.

This may be readily determined, and at the same time an accurate check on the method obtained, by precipitating as AgCl the chlorine in the calcium chloride solution obtained in each experiment.

The directions given by Fresenius for the precipitation of chlorides by slight excess of silver nitrate in presence of nitric acid were followed closely, the filter-paper being burnt separately and the bulk of the precipitate then added, and finally heated to fusion at the edges, after treatment with HNO_3 and HCl, though it had as far as possible been kept in a dark room, and showed merely the slightest signs of darkening.

Comey ("Dictionary of Solubilities") states that silver chloride is slightly soluble in sodium and calcium nitrates. No data are given for calcium nitrate, but a solution of sodium nitrate of about the strength employed will dissolve 20—25 mgms. of silver chloride per litre.

As calcium chloride has very nearly the same capacity as sodium chloride for dissolving AgCl, I have, in the absence of any exact data, felt justified in assuming the solubility of freshly precipitated AgCl to be 24 m.grms. per litre of filtrate. In pure water the solubility is given as 1·8—2·0 m.grms. per litre at ordinary temperatures.

The volumes of the filtrates and washings were noted and corrections applied on the above basis, but in view of the uncertainty involved, the uncorrected values are given for comparison.

In calculating the molecular weight of the Iceland spar the accuracy of the method and the purity of the reagents have been assumed, and the correction for the solubility of AgCl has been introduced. (Taking Ag = 107·93, Cl = 35·45, and $CaCO_3$ = 100·00, then 2·8676 grms. of AgCl should be obtained for each grm. of $CaCO_3$ dissolved). (See Table III.).

In considering these results it must be borne in mind that the determination of the atomic weight of calcium was not the object of these experiments, and that only analytical precautions were taken, the following sources of error not being accounted for:—

1. Ordinary clear fragments of Iceland spar were employed, and any impurities they may have contained were not determined. (The Iceland spar used by Erdmann and Marchand, in determining the atomic weight of calcium, contained 0·04 per cent impurities.)

2. The silver nitrate and hydrochloric acid employed were "pure" reagents and were not specially purified.

3. The solubility of silver chloride in calcium nitrate solutions was not investigated, and only approximately corrected for.

TABLE III.

Vessels employed.	Total loss of glass and spar.	Loss in weight of glass. M.grms.	Iceland spar dissolved.	Strength of HCl from each pair of vessels.	Weight of AgCl. Uncorrected.	Weight of AgCl. Corrected for solubility.	Strength of HCl calculated from AgCl. Uncorrected.	Strength of HCl calculated from AgCl. Corrected for solubility.	Weight of AgCl per grm. of spar dissolved. Uncorrected.	Weight of AgCl per grm. of spar dissolved. Corrected for solubility.	Molecular weight of Iceland spar.
V. } Bohemian glass beakers ..	0·9988	0·65	0·99815	0·998075	2·8572	2·8608	0·99643	0·99770	2·8625	2·8661	100·053
VI. }	0·99845	0·45	0·9980		2·85755	2·86115			2·8633	2·8669	100·025
VII. } Conical parting flasks ..	0·9995	1·4	0·9981	0·9980	2·8584	2·8618	0·99664	0·99783	2·8638	2·8672	100·014
VIII. }	0·99945	1·55	0·9979		2·8576	2·8610			2·8636	2·8670	100·021
IX. } Jena glass flasks . ..	0·99845	0·35	0·9981	0·998025	2·85915 (*a*)	2·86225	0·99680	0·99787	2·8646	2·8677 (*a*)	
X. } ..	0·9984	0·45	0·99795		2·8581	2·8612			2·8640	2·8671	100·017
				0·99803			0·99662	0·99780	2·8635	2·8669	100·02

(*a*) The AgCl in IX. was known to be slightly too high, owing to the presence of a fragment of unburnt filter-paper; consequently this result was not used in calculating the average values.

4. The weighings were not reduced to vacuum. The corrections, if applied, would amount on the spar to 0·3 m.grm. per grm., and on the silver chloride to 0·1 m.grm. per grm.; but it must be observed that variations in the atmospheric conditions could easily be sufficient to cause differences in the apparent weight of the beakers of over 0·1 m.grm.

5. The weights were not corrected, and errors amounting to tenths of m.grms. were known to exist.

6. Glass vessels which lost weight during the experiment were employed, and though this loss was determined so as to obtain the true loss of weight of the spar, a minute error is still possible if any portion of the acid were neutralised by the alkali of the glass.

The results obtained may, however, be held to prove that for the purposes of standardising hydrochloric acid solutions (and also for obtaining a standard solution of neutral calcium chloride) in the laboratory, the molecular weight of Iceland spar may be taken as 100·0, and that the accuracy of the measurement of the acid will, in practice, determine the accuracy of the standardisation.

For extreme accuracy the precautions indicated as to the use of Jena flasks previously extracted by boiling in acidulated water must be attended to.

Without question, the method is preferable to any other in common use.

The University of Melbourne, October 1, 1902.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1902.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, December 10th, 1902.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 206 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 1st to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 206 samples examined by us chemically during the month, all were clear, bright, and well filtered.

The rainfall at Oxford has been again below the average; the rainfall actually measured during November is 2·24 inches, the average is 2·30 inches; this leaves a deficit of 0·06 inch, and when added to the previous one of 7·84 inches, makes a total deficit of 7·90 inches, or 34·1 per cent on the thirty-five years' average.

Our bacteriological examinations of 508 samples have given the results recorded in the following table; besides these we have examined 109 other samples, from special standpipes, wells, &c., making a total of 617 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	277
New River, filtered (mean of 123 samples) ..	16
Thames, unfiltered (mean of 25 samples) ..	2262
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 279 samples)..	35
Ditto ditto .. .. highest	452
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 25 samples) ..	253
River Lea, from the East London Company's clear-water wells (mean of 32 samples) ..	13

Of the 434 daily samples taken from the filter-wells of the Metropolitan Water Companies, and examined bacteriologically by us, eleven samples, or 2·5 per cent, were sterile. Fourteen samples contained more than 150 microbes, while twenty-seven samples, or 6·2 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the twenty-seven excess samples was 165, against a corresponding mean of 145 in twelve excess samples in October.

The small increase in the number of microbes during November is no doubt due to the larger rainfall. Past experience has shown that, but for the exceptional season, we should have anticipated that the supplies ere this time would have exhibited a more marked increase in vegetable organic matter and harmless microbes. The quality of the water supply is excellent, and is better than the average of the usual winter standard.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE USE OF ACID NITRATE OF MERCURY IN THE ANALYSIS OF SUGAR LIQUORS.

By G. PATEIN and E. DUFAU.

THE analysis of sugar liquors offers a certain number of difficulties, among which is the elimination of impurities which accompany the sugar under examination, especially when these substances have a rotatory power, or when they reduce Fehling's solution and decolourise or modify the colour of that reagent. The treatment of the liquor to be analysed by subacetate of lead has long been recommended, followed by the precipitation of the excess of lead by sulphate or carbonate of soda; but, since it has been seen that this process might bring about a loss of sugar, recourse has been had to the neutral acetate of lead, and Courtonne's solution has come into general use. This latter reagent, as has been shown by us, though excellent in most cases, is itself incapable of precipitating certain nitrated compounds which are often met with in the liquors, and which can only be removed by the acid nitrate of mercury.

But though the mercurial salt was well received it was not accepted universally, and MM. Lépine and Boulod condemned it in a sentence we came across in several journals (*Review de Médecine*, 1901, p. 633; *Lyon Medical*, 16 June, &c.)* in which they published their work, as well as in the *Bulletin des Sciences Pharmacologiques*, 1901, p. 399.

It has been known for a long time that the mercuric salts are able to oxidise sugars, and the methods of estimation of Knapp, Pillitz, and Sacchsse are well known, but to effect this both heat and the presence of alkalis are necessary; time and direct sunlight act in the same

* M. Patein has proposed to treat urine with acid nitrate of mercury, before polarimetric examination; but it has been found by one of us (M. Boulod) in a special series of tests, that the use of the acid nitrate of mercury is to be condemned entirely; this salt destroys a portion of the sugar.

manner. Again, we have distinctly specified that it is necessary to add only the amount of soda that is actually necessary to effect neutralisation. Furthermore, it will be seen in what follows how sugars dissolved in water really behave in the presence of mercuric nitrate. For these experiments we have used nothing but chemically pure products.

Primarily we have observed that if we make a very dilute solution of *glucose*, say 0·2 grm. per litre, by using the acid nitrate with the given precautions, we can detect the presence of sugar with the aid of Fehling's solution as distinctly as in a solution not treated with the mercurial reagent; thus, the use of this latter is perfectly well justified for very dilute solutions of sugar. If, on the other hand, the sugar is oxidised, we ought to find a corresponding quantity of the mercurial salt reduced. To try and find if this is the case, we carried out the following experiments on different sugars:– 1 grm. of sugar was dissolved in 50 c.c. of water; 10 c.c. of the solution of mercuric nitrate was added, of which we give the formula further on; then soda drop by drop until the acid reaction has disappeared; filter, and after filtration it was found that the filtrate which remained perfectly limpid did not give any precipitate with hydrochloric acid—therefore it did not contain any mercurous salt; as for the precipitate remaining on the filter, this was collected and dissolved in dilute hydrochloric acid; the solution was not quite complete, but the residue, which consisted of mercurous chloride, was very slight; when collected, washed and dried, its weight varied from 2 to 5 grms. A check solution, not containing any sugar, and treated in the same manner as the other one, also gave a residue of mercurous chloride weighing 2 grms. Thus, we are justified in stating that the oxidising action of the acid nitrate of mercury on reducing sugars does not show itself to any noticeable extent, if our instructions are followed.

We have also verified the fact that, even if it is not neutralised, nitrate of mercury does not invert the hydrolysable sugars, and does not modify the rotatory power of any of the sugars with which we have had to deal.

That being settled, we will give the most complete details of the method of working we have employed.

1. *Preparation of the Mercuric Reagent.*—The formula we originally gave may be adhered to and the ordinary acid nitrate used; however, among other impurities, this salt generally contains a little mercurous nitrate, and, to obtain a solution free from this body we prefer to proceed in the following manner:—

We take 220 grms. of the yellow oxide of mercury and treat it with 200—300 c.c. of water, and the exact quantity of nitric acid necessary to effect its solution; a few drops of soda-lye are added until a yellowish precipitate just appears, the volume is made up to a litre and the solution filtered. This solution does not contain any excess of nitric acid, and the amount of mercurous salt present is negligible.

2. *Soda Solution.*—Soapmaker's lye is used, treated with four times its volume of water; the liquid is left in a glass vessel, and the carbonic acid of the air does not interfere with it in any way.

3. *Method of Working.*—We will describe, as an example, one of our estimations of glucose. We took a solution containing 4·50 grms. of pure anhydrous glucose in 100 c.c. of water. We measured off successively 20 c.c. into two test-glasses graduated to 50 c.c.; in one of them this volume was made up with water, and to the other we added 10 c.c. of the mercuric reagent and 10 c.c. of water; after well stirring, and by means of a burette, the soda solution was added drop by drop, with continual stirring with a glass rod, taking care to stop for a while after each five or six drops, to allow the precipitate to settle; if the soda-lye is not carbonated, this precipitate will be first white, then yellowish, and gradually become darker; if, on the other hand, it is strongly carbonated, the precipitate is much more brown in colour. But however it may be, we continue to add the sodic liquor until one drop of the clear solution does not turn blue litmus-paper red; the volume is then made up to 55 c.c. with distilled water, shake well, and filter. If the operation has been carried out properly, the solution is neutral or at least barely alkaline; it is, and remains, perfectly limpid; it is not precipitated by hydrochloric acid nor by the addition of a drop of the sodic solution. As for the precipitated mercuric oxide, it ought to dissolve almost integrally in dilute hydrochloric acid; the insoluble residue of mercurous chloride was 3 c.grms. On examining our two solutions in the saccharimeter we found 8·7° or 17·72 grms. of glucose per litre for the one simply diluted with water, and, for the one treated with mercuric nitrate, 8·6°, or 17·71 grms. of glucose per litre; the actual amount taken was 18 grms. per litre.

	Solution in pure water.	Solution treated with mercuric nitrate.	Solution treated with peptone and then with nitrate.	Solution treated with nitrate and then with hypophosphite.
Saccharose—				
Polarimetry	11·4°	11·3°	11·3°	hydrolysed
	8·6°	8·6°	8·5°	—
Fehling ..	—	—	—	—
Lactose—				
Polarimetry	11·5°	11·5°	11·5°	11·5°
	9·4°	9·3°	9·3°	9·3°
Fehling ..	11·8 c.c.	—	—	12·0 c.c.
	7·8 c.c.	—	—	7·9 c.c.
Maltose—				
Polarimetry	9·5°	9·4°	—	9·4°
	9·4°	9·3°	—	9·3°
	4·8°	4·7°	—	4·7°
Fehling ..	17·8 c.c.	—	—	18·2 c.c.
	9·6 c.c.	—	—	9·8 c.c.
Glucose—				
Polarimetry	8·4°	8·3°	8·3°	8·3°
	8·8°	8·7°	8·7°	—
	4·1	4·1°	4·1°	—
Fehling ..	9·0 c.c.	—	—	9·1 c.c.
	6·1 c.c.	—	—	6·2 c.c.
Levulose—				
Polarimetry	−7·5°	−7·5°	—	−7·5°
	−6·4°	−6·3°	—	−6·3°
Fehling ..	10·3 c.c.	—	—	10·4 c.c.
	8·8 c.c.	—	—	8·9 c.c.
Arabinose—				
Polarimetry	7·5°	7·5°	—	—
	7·5°	7·4°	—	7·4°
Fehling ..	11·3 c.c.	—	—	11·4 c.c.
	11·4 c.c.	—	—	11·6 c.c.

4. *Volumetric Estimation.*—If we wish to estimate the glucose by means of Fehling's solution in the above solution, treated with mercuric nitrate, we obtain too low a result. Does this come from any destruction of sugar? Not at all; it arises from the fact that the sugar liquor always retains some of the mercuric salt in solution, and when we pour in the boiling Fehling's solution the sugar is oxidised both by the latter and by the mercuric salt, as is proved by the black colour taken by the cuprous oxide. It is necessary, therefore, to commence by eliminating the mercury, and this precaution is equally indispensable in the processes in which the oxide of copper is weighed or the copper reduced, and in which a salt of mercury has been used to purify the sugar. It is on account of the constant presence of mercury in solution that we have recommended, for the polarimetric examination, the use of tubes lined with glass, or else the precipitation of the mercury by hypophosphite of soda according to Maquenne's method. Hypophosphite of soda in boiling alkaline solution, partly decolourising the Fehling's solution, does not seem suitable for use in volumetric estimations. However, we obtained the most satisfactory results in the following manner:—To 50 c.c. of the sugar

liquor treated with mercuric nitrate, we add two drops of hydrochloric acid, then 8 c.grms. of hypoposphite of soda, and heat for a moment to 60—70°, the solution first becomes cloudy, then a precipitate is formed which agglomerates or becomes granular, floating in the clear liquid; after cooling this is filtered; the filtrate is absolutely free from mercury, and does not contain more than a few milligrms. of hypophosphite, which have no influence on the estimation. The action of heat is sufficiently slight and of short duration not to change the volume of the solution or to effect any hydrolysis of the sugars, except with saccharoses.

To make the estimation with Fehling's solution, the solution is neutralised and diluted so as to contain about 5 grms. of sugar per litre. In this manner we have found with the experimental solution, that to decolourise 10 c.c. of Fehling's solution it required, after dilution, 7·7 c.c. of simple glucose and 7·9 c.c. of the solution treated with mercuric nitrate.

The accompanying table shows the results we have obtained with different sugars; our experiments have been far more numerous than those we describe here.

We see that the variations caused by the acid nitrate of mercury are not great; glucose appears to be the most sensitive sugar, and the neutralisation with soda ought to be done with the greatest care; levulose, maltose, and lactose are much less sensitive. This method of treating sugar liquors, therefore, is not to be passed over; in a future paper we shall show that in certain cases it is even necessary.—*Journ. de Pharm. et Chim.*, Series 6, vol. xv., No. 5.

VOLUMETRIC ESTIMATION OF DISODIC METHYLARSENATE.

By ELIE FALIÈRES.

I HAVE determined the conditions under which methylarsenate of silver ought to be used for the estimation of the new salt described by Prof. Armand Gautier. I have been enabled thus to devise a method for the volumetric titration of disodic methylarsenate, of which the accuracy is absolutely equal to that of an estimation of alkaline chlorides, with which it is connected.

Methylarsenate of silver,—

$$CH_3—As\begin{matrix}=O\\-OAg\\-OAg\end{matrix},$$

is almost insoluble in water, but though slight its solubility is sufficient to interfere with the correctness of the estimation of the silver salt when washed and dried, in comparison with a sample of disodic methylarsenate.

The wash-waters from the methylarsenate of silver are, in fact, indefinitely and distinctly precipitable by hydrochloric acid or chlorides. It is impossible to know when to stop washing the precipitated methylarsenate of silver. The results are always too low and vary according to the duration and amount of the washing.

But though the methylarsenate is not insoluble in water, it is, on the other hand, completely insoluble in a solution of N/10 or even N/20 nitrate of silver. In this case its insolubility is as absolute as that of sulphate of barium of chloride of silver.

I have proved this insolubility experimentally by leaving a demi-decinormal solution of nitrate of silver for several hours in contact with precipitated, thoroughly well-washed and well-drained methylarsenate of silver. The silver solution has not dissolved the least trace of the methylarsenate; its titrated strength, after filtration, remained exactly the same, viz., demi-decinormal.

The same is the case with decinormal nitrate of silver.

Pure disodic methylarsenate crystallises regularly with 6 molecules of water, which it loses completely at a temperature of 120—130°, and which it takes up again to a very great extent by simple exposure to the air.

The rapidity with which the anhydrous salt becomes hydrated, no doubt accounts for the differences in the number of molecules of water of crystallisation which have been variously attributed to this salt when crystallised; 143 m.grms. of anhydrous disodic methylarsenate weighed rapidly on taking from the oven, gained 20 m.grms. of water in five minutes; 32 m.grms. in twenty minutes; 41 m.grms. in forty minutes; and 45 m.grms. in forty-five minutes. These figures show that unless we take precautions in weighing, altogether beyond the precautions usually necessary, it is of no use to take the anhydrous or supposed anhydrous salt in making an estimation. It is preferable to take the salt $As(CH_3)O_3Na_2,6H_2O$, of which the composition remains constant even after being exposed to the air for several days. The atomic weight of the anhydrous salt is 184, that of the crystalline salt 292. The normal crystalline salt contains 37 per cent of water and 25·68 per cent of arsenic.

We must first make sure that the methylarsenate to be determined does not contain any of the following salts:—Chlorides, sulphates, arsenites, arsenates, phosphates, carbonates, or iodides.

0·2 grm. of the crystalline salt is weighed out and dissolved in exactly 10 c.c. of water. 40 c.c. of a decinormal solution of neutral nitrate of silver are added, thus:—

$$0·017 \text{ grm.} \times 40 = 0·68 \text{ grm. } NO_3Ag.$$

After stirring thoroughly it is filtered rapidly. The filtrate, having a total volume of 50 c.c., including the portion absorbed by the filter-paper and the precipitate itself, contains the whole of the nitrate of silver, which has not been used for the precipitation of the methylarsenate of silver.

We then determine how many cubic centimetres of this filtrate must be used to obtain the tint of chromate of silver with 10 c.c. of N/10 chloride of sodium diluted with 30 c.c. of distilled water.

Ten c.c. of N/10 chloride of sodium correspond to 0·17 grm. of nitrate of silver, so by a simple calculation we find the weight A of the nitrate of silver still remaining in the 50 c.c. of the liquid under examination. This weight A subtracted from 0·68 grm. gives the weight N of the nitrate of silver precipitated in the form of methylarsenate of silver.

By applying the formula $\frac{292 \times N \times 5 \times 100}{340}$ we get the value in hundredths of the disodic methylarsenate in question; 292 = a molecule of disodic methylarsenate, 340 = a double molecule of nitrate of silver, 5 = multiplying the amount taken by 0·2 grm.

The results are extremely accurate, and absolutely concordant on several estimations of the same sample.

Analytical Results.

Pure Salt in the Laboratory.—N = 0·232, from which we get $\frac{292 \times 0·232 \times 5 \times 100}{340} = 99·91$ per cent.

Salts from various Sources.—(A). N = 0·226—

$$\frac{292 \times 0·226 \times 5 \times 100}{340} = 97·01 \text{ per cent.}$$

(B). N = 0·223—

$$\frac{292 \times 0·223 \times 5 \times 100}{340} = 95·93 \text{ per cent.}$$

(C). N = 0·231—

$$\frac{292 \times 0·231 \times 5 \times 100}{340} = 99·17 \text{ per cent.}$$

—*Journ. de Pharm. et Chim.*, Series 6, vol. xv., No. 10.

NOTICES OF BOOKS.

Notions Fondamentales de Chimie Organique ("Fundamental Notions of Organic Chemistry"). By Ch. Moureu. Paris: Gauthier-Villars. 1902.

This is a text-book dealing with the general theory of organic chemistry, all questions of detail and the study of individual substances being designedly omitted. If extensive practical work in organic chemistry is done, the student undoubtedly learns more satisfactorily the details of the subject by studying the preparation and properties of the more common substances in the laboratory by practical methods, and acquires a more comprehensive view of the whole subject by reading in his text-book only of groups of bodies of the same type. This ideal method unfortunately has often to be very considerably modified in order to save time. This book will be found in many ways most useful, the general plan being on the whole excellent. We should not advise its use, however, as suggested in the preface, as an introduction to a complete course or treatise, but in conjunction with some good practical book and constant laboratory work. The contents are divided into six chapters, the first being introductory and discussing general theories of isomerism and stereo-chemistry; the student then takes up the hydrocarbons and compounds containing oxygen and nitrogen, thence proceeding to organo-metallic and heterocyclic bodies. The chapter on nitrogen compounds is specially well written, but the methods of preparing hydrocarbons might have been made more complete with advantage.

Die Chemische Technologie der Brennstoffe ("The Chemical Technology of Fuels"). By Dr. Ferdinand Fischer. Braunschweig: Friedrich Viewig und Sohn. 1901.

This volume of the hand-book of chemical technology now in course of publication deals with the chemistry of all classes of fuels; the author has endeavoured to produce a clear and comprehensive exposition of his subject. The volume is copiously illustrated throughout, and the illustrations are in many cases very elaborate in detail; in places the text requires substantial additions to bring it up to date. Though the practical side of the subject is most emphasised, the scientific side is not by any means neglected; the chapters on producer-gas and water-gas are among the best in the book.

Wellenlängen-Tabellen für Spektralanalytische Untersuchungen auf Grund der Ultra-violetten Funken Spektren der Elemente ("Wave-length Tables for Spectral Analysis on the basis of the Ultra-violet Spark Spectra of the Elements"). By Professor Franz Exner and Dr. E. Haschek. Leipzig und Wien: Franz Deuticke. 1902.

This collection of tables of wave-lengths for spectral analysis will undoubtedly supply a want. The compilers have made the determinations with the greatest possible accuracy, using the same method throughout. The elements examined include all at present known with the exception of terbium and of the rare gases argon, helium, &c. The tables are three in number, and fill two volumes; the first gives the principal lines of the elements arranged alphabetically under their symbols, and will be found useful in showing rapidly whether a given element is present in an unknown spectrum. The second table gives all the lines arranged in ascending order of wave-length of all the elements, and thus provides a means of identifying unknown lines. The third table, which fills the whole of the second volume, gives the complete spark spectra of all the elements, each element being prefaced by a few notes explaining whether the electrodes consisted of the element itself, or of carbon saturated with a solution of a compound, and also giving the most probable impurities present. The compilers hope to prepare shortly similar tables of the arc spectra of all the elements.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 23, December 8, 1902.

Transformation of the Diamond into Black Carbon during its Oxidation, and the Isomeric Changes of Simple Bodies during Decompositions and Combinations.—M. Berthelot.—During a series of experiments made some years ago to determine the heat of combustion of carbon in different states, and especially that of the diamond, the author burnt diamonds incompletely in pure dry oxygen in crucibles placed in porcelain or hard glass tubes. The amount of amorphous carbon produced by this method was always very small, too small in fact to allow of a study of its isomeric state. However, it seemed probable that from his experiments that it contained some graphite.

The Quantity of Pure Hydrogen in the Air and the Density of Atmospheric Nitrogen.—Armand Gautier.—The presence of free hydrogen in the atmosphere is important from the point of view of the origin of the air, its constitution, the constitution of the upper layers of the atmosphere, and the part which this gas takes in meteoric and chemical phenomena. It is certain that the composition of the air is slightly variable, and the weight of unit volume is not the same in the country, in populous towns, over the sea, and in the higher regions of the atmosphere.

Bipolar Electrodes with Soluble Anode.—André Brochet and C. L. Barillet.—The authors' researches on bipolar electrodes lead them to the following conclusions: —(1) Bipolar electrodes with soluble anode change the flow of the current because of important phenomena of polarisation. (2) A useful application of bipolar electrodes necessitates that they form water-tight partitions; the spaces reserved for the circulation of the liquid should be as small as possible to avoid the loss, which is considerable with soluble anodes. (3) If the apparatus necessitates a violent agitation to make the electrolyte circulate transversely between the electrodes in all compartments at a time, the electrodes should be introduced into frames of large dimensions. (4) In an electrolyser it is best to use metallic strips not communicating with the electrodes.

Thallic Chloride.—V. Thomas.—In a previous paper the author described in a general manner the halogen compounds of thallium of the type ThX_3. Amongst others he shows the easy formation of the compounds corresponding to the formulæ—$ThCl_3.4H_2O$, $ThCl_2Br.4H_2O$, $ThClBr_2.4H_2O$, and $ThBr_3.4H_2O$. These compounds are all characterised by the ease with which they combine with one molecule of hydracid. If the two extreme members of the series represent well-defined chemical substances, the intermediate members must be looked upon as mixtures of chlorides and bromides—

$$3ThCl_2Br.4H_2O = 2ThCl_3.4H_2O + ThBr_3.4H_2O,$$
$$3ThClBr_2.4H_2O = 2ThBr_3.4H_2O + ThCl_3.4H_2O.$$

The author now makes a study of the trichloride, $ThCl_3.4H_2O$, and finds (1) that anhydrous thallium trichloride is capable of existence, and (2) that thallic chlorobromides do exist, from the fact that in a vacuum they lose both chlorine and bromine.

The Violet Manganic Metaphosphate of Gmelin.—Ph. Barbier.—M. Laspeyre, repeating Gmelin's researches, obtained a dark violet syrupy mass soluble in water, giving a ruby-red colouration. The solution becomes decolourised as it is heated, an insoluble greenish-grey powder being deposited. The author repeats this experiment, and makes a further examination of the product.

MEETINGS FOR THE WEEK.

SATURDAY, Jan. 3rd, TUESDAY, 6th. THURSDAY, 8th. } Royal Institution, 3. (Christmas Lectures, adapted for Young People). "On Locomotion—on the Earth, through the Water, in the Air," by Prof. H. S. Hele-Shaw, LL.D., F.R.S., M.Inst.C.E.

MONDAY, 5th.—Society of Chemical Industry, 8. "Fluorescence of Naphthalic Anhydride," by Dr. J. T. Hewitt. "Saponification of Fats and Oils by means of Dilute Acids," by Dr. J. Lewkowitsch

WEDNESDAY, 7th.—Society of Arts. 5. (Juvenile Lecture). "Means of Defence in the Struggle for Life among Animals," by Prof. E. B. Poulton, F.R.S.

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THE CHEMICAL NEWS.

Vol. LXXXVII., No. 2250.

ISOMERIC CHANGE IN BENZENE DERIVATIVES.*

The Interchange of Halogen and Hydroxyl in Benzenediazonium Hydroxides.

By K. J. P. ORTON, Ph.D., M.A., St. John's College, Cambridge, Demonstrator of Chemistry, St. Bartholomew's Hospital.

In discussing the laws which govern substitution in the case of benzenoid compounds, Armstrong, in 1887, drew special attention to the peculiar behaviour of amido- and hydroxy-compounds, from which he inferred that the phenomena of substitution were less simple than was commonly supposed. He showed that there was evidence that the formation of para-derivatives was preceded by that of an isomeric compound formed by the displacement of the aminic hydrogen or hydroxylic hydrogen, and pointed to the probability that this might prove to be true also of ortho-compounds.

Since that time, it has been experimentally demonstrated by various chemists that the radicles, Cl, Br, I, NO_2, SO_3H, can all be introduced in place of the hydrogen of the amino-group of anilines and of the imino-group of anilides, and that the compounds thus formed can be changed into isomeric substances in which the substituent is contained in the hydrocarbon nucleus.

The transformation of the aniline derivative appears to take place only in the presence of some other substance: in the case of the phenylacylchloramines, such as $C_6H_5.NCl.COCH_3$, for example, apparently the change into the isomeric chloroacetanilides takes place only under the specific influence of hydrogen chloride (Compare Armstrong, *British Association Report*, 1899, p. 683; *Trans. Chem. Soc.*, 1900, vol. lxxvii., p. 1053). The investigation of such cases of isomeric change is, in fact, of special interest, as they are, so to speak, "fermentative" in character, often taking place with remarkable facility, and under the influence of minute amounts of the substance, which apparently provokes the change—the catalyst. Measurements of the velocity at which changes of this type occur, for example, of diazoaminobenzene into aminoazobenzene (Goldschmidt and Reinders, *Berichte*, 1896, vol. xxix., p. 1369), show that a velocity-coefficient of constant value is given by the equation—

$$k = t^{-1} \log a/(a-x).$$

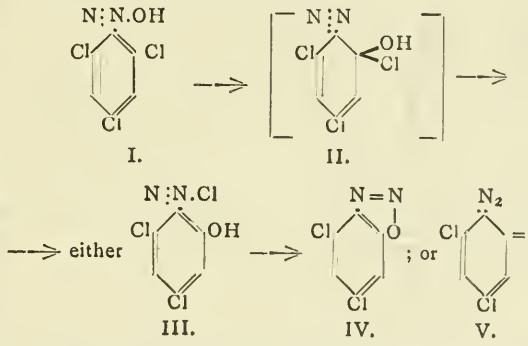
The isomeric change is, therefore, apparently a so-called monomolecular change; but, as in other cases, the slowest of the series of simple changes which make up the complete transformation is alone measured; moreover, the substance which conditions the change is not taken into account.

This paper deals with a new case of intramolecular change of a particularly interesting character: that of *s*-trichloro- and *s*-tribromobenzenediazonium hydroxide, $C_6H_2X_3.N(OH):N$, into hydroxybenzene derivatives, by the interchange of the hydroxyl for one of the ortho-halogen atoms. The change takes place under all conditions under which it is possible for the diazonium hydroxide to be present. Thus, in dilute aqueous solutions of the neutral diazonium nitrate, or even of the hydrogen sulphate, chloride is just recognisable by means of silver nitrate after twenty-four hours; at the same time the solution becomes yellow, owing to the formation of the diazophenol. But as the extent to which the nitrate, and more especially the sulphate, undergoes hydrolytic dissociation is extremely small, the isomeric change takes place very slowly; and in the presence of a considerable excess of acid no appreciable change occurs during five days. On the other hand, using diazonium acetate, 50 per cent of the material changes within thirty to forty hours; and in the case of diazonium bicarbonate the change is nearly instantaneous. That the change is a transformation of the diazonium hydroxide is further emphasised by the fact that the addition of a solution of the diazonium salt to a considerable excess of an aqueous solution of an alkali carbonate, is not followed by elimination of halogen; the solution remains colourless, the diazonium salt being immediately converted into the alkali diazotate.* The latter change may be represented thus—

$$\underset{\text{Diazonium salt.}}{C_6H_2X_3.NR{:}N} \rightarrow \underset{\text{Diazonium hydroxide.}}{C_6H_2X_3.N(OH){:}N} \rightarrow C_6H_2X_3.N{:}N{\cdot}OM'.$$

Diazotate.

As the author has maintained on previous occasions, the first step in this type of intramolecular change consists in a transference of the atom or group attached to the nitrogen to the ortho- or para-carbon atom of the nucleus, an ortho- or para-quinone being formed. The complete transformation in the case here described may be represented in the following manner:—



In other words, the diazonium chloride (III) may be represented as changing into the "diazophenol" (IV); or, if, following Wolff (*Annalen*, 1900, vol. cccxii., p. 119) and Hantzsch (*Berichte*, 1902, vol. xxxv., p. 888), the diazophenols are considered to be diazoquinones (V), the ortho-quinone form (II) merely loses hydrogen chloride.

Closely allied to the intramolecular change just mentioned, are Hantzch's observations (*Berichte*, 1896, vol. xxix, p. 947; 1897, vol. xxx., p. 2334; 1898, vol. xxxi., p. 1253; 1900, vol. xxxiii., p. 505) that *s*-tribromobenzenediazonium chloride changes into chlorodibromobenzenediazonium bromide, and chloro- and bromobenzenediazonium thiocyanates into thiocyanobenzenediazonium chlorides and bromides.

(The following observations of Meldola (*Proc. Chem. Soc.*, 1901, vol. xvii., p. 131; *Trans. Chem. Soc.*, 1902, vol. lxxxi., p. 988) may also be mentioned, as the author's results offer a possible explanation. When dinitro-*o*- or dinitro-*p*-anisidine is treated with sodium nitrate in the presence of acetic acid, the nitro-group, occupying a position, ortho or para with respect to the amino-group, is eliminated, a diazophenol (diazo-oxide) being formed. In diazotising in the presence of hydrogen chloride, an ortho-nitro group is replaced by chlorine.)

The isomeric changes of the diazonium salts differ,

* A Paper read before the Royal Society, December 4, 1902.

* Professor Meldola has called the author's attention to a French patent (No. 315,932) of the Badische Aniline Company, dated Feb. 28, 1902, in which the replacement of the nitro-group and halogen by the hydroxyl-group *by the action of alkalis* on diazonium salts, is claimed as a technical process. The author's experiments show within what limits this process is applicable, and what is the probable action of the alkali.

however, somewhat from the similar changes of the phenylacylchloramines, phenylnitramines, &c. The latter compounds are *per se* relatively stable, and apparently only undergo changes in the presence of some agent (catalyst); the diazonium compounds, on the other hand, appear to be intrinsically labile, and in aqueous solution, at least, capable of passing into a more stable configuration. In the latter case the nitrogen atom, bearing the wandering group, the hydroxyl group (or, as in Hantzsch's instances, the chlorine atom or the thiocyanate group), is pentad, thus, $Ph.N(OH):N$, whilst in the phenylacylchloramines, &c., it is triad. The idea at once suggests itself that in the case of the last-mentioned compounds, the first action of the catalyst is to form an additive product, in which the nitrogen is pentad. The product, in which, it should be noted, more than one negative radicle is attached to the nitrogen, is not a stable compound, and is now capable of passing into the isomeric quinone form, and thus start the transformation.

These results are also of interest, inasmuch as Hantzsch (*Berichte*, 1902, vol. xxxv., p. 2964) has stated recently that he has obtained *s*-tribromophenylnitrosamine, $C_6H_2Br_3.NH.NO$, by adding sodium acetate to a solution of a *s*-tribromobenzenediazonium salt. He describes it as a bright yellow amorphous substance, which decomposes at 85°. As far as can be judged, it is this very reaction which has been studied in the course of the author's experiments. The substance which is precipitated is at first glance a yellow amorphous powder, but close observation shows that long (½—1 c.m.) orange crystals are present. These crystals are the 3:5-dibromo-*o*-diazophenol hereafter described. The powder is probably a hydroxyazo-condensation product. Hantzsch does not appear to have observed that bromine is eliminated. He also affirms (*loc. cit.*) that he obtained the nitrosamine by the cautious addition of acetic (or other) acid to the alkali diazotate; in the writer's experience, however, this always leads to the elimination of halogen.

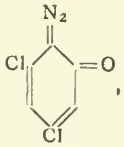
The Transformation of s-*Trichlorobenzenediazonium Hydroxide.*

s - *Trichlorobenzenediazonium hydrogen sulphate*, $C_6H_2Cl_3.N(SO_4H):N$, is very easily prepared by diazotising, by means of amyl nitrite, *s*-trichloraniline dissolved (or suspended) in glacial acetic acid containing sulphuric acid. The salt is precipitated by ether, and is purified by dissolving in methyl alchohol; on adding ether to this solution the sulphate separates in small colourless lustrous prisms, often forming star-shaped aggregates, which are very soluble in water (SO_4—found 31·0, calculated 31·4 per cent). s - *Trichlorobenzenediazonium nitrate*, $C_6H_2Cl_3.N(NO_3):N$, prepared in a similar manner, forms colourless needles. When kept for two or three days, both salts begin to show signs of change, which are more marked in the case of the nitrate. The latter becomes noticeably yellow, and when dissolved in water forms a yellow solution. The initially colourless aqueous solution of the pure colourless salts becomes yellow after a few hours; after twenty-four hours chloride is just recognisable in the solution. In one experiment, 0·5 grm. of the acid sulphate was dissolved in 100 c.c. of water; after three days a very small amount of a yellowish red solid had separated from the yellow solution; at the end of sixteen days, the chloride in solution was precipitated by silver nitrate in the presence of nitric acid: the silver chloride weighed 0·05 grm., whereas for the complete conversion of the diazonium salt into the diazophenol, 0·235 grm. of silver chloride should have been found.

An aqueous solution of *s*-trichlorobenzenediazonium acetate, obtained by mixing neutral solutions of the diazonium nitrate and sodium acetate (molecular proportions) rapidly becomes yellow and acid. In a short time the solution becomes turbid, and after four to five hours deposits a bright yellow amorphous solid. In an experiment, in which 1·75 grms. of the diazonium nitrate, dissolved in 150 c.c. of water, was treated with sodium acetate (1 mol.), and kept at 10—15° for forty hours in the dark, an estimation of the hydrogen chloride in the solution showed that 54·5 per cent of the diazonium compound had changed into the diazophenol.

When instead of sodium acetate, sodium hydrogen carbonate was used, a similar change took place, but far more rapidly. In one experiment a dilute aqueous solution of sodium hydrogen carbonate (3 mol.) was added drop by drop during a period of one hour to a cooled solution of 1 grm. of the diazonium hydrogen sulphate. (The bicarbonate was finally present in sufficient quantity to combine with the whole of the sulphuric acid and one-third of the chlorine present in the diazonium salt). After one-third of the bicarbonate had been added, and the acid converted into the normal sulphate, the solution rapidly became yellow and deposited a yellow solid. Throughout the experiment the mixture was acid. As soon as the whole of the bicarbonate was added, the chlorine was estimated; it represented 54·5 per cent of the amount which should be obtained were 1 atom of chlorine eliminated from the diazonium salt. In another experiment, using the same quantities of diazonium salt and sodium bicarbonate, the solutions were mixed as rapidly as possible; a copious yellow precipitate at once appeared; the chloride in the filtrate represented 72 per cent of 1 atomic proportion of chlorine.

3 . 5-*Dichloro* o-*diazophenol* (3 . 5-*dichloro*-o-*diazoquinone*),—



is contained in the yellow solutions which are obtained by any of the methods just described. It is best prepared by adding excess of sodium acetate to *s*-trichlorobenzenediazonium hydrogen sulphate or nitrate. The mixture should be kept during forty to fifty hours in the dark; in the light the solution darkens, the diazophenol decomposing. The liquid was then filtered from the amorphous yellow solid, made strongly acid with nitric acid, and extracted four or five times with ether. On evaporating the yellowish-brown extract, a mixture of oil and crystals remained. In order to obtain the diazophenol, dry hydrogen chloride was passed into the ethereal extract; this caused the *hydrochloride* of the dichloro-*o*-diazophenol, $O:C_6H_2Cl_2:N_2,HCl$, to separate in small needles. This salt was converted into the diazophenol by treatment with a small quantity of water. Thus prepared, the diazophenol is an orange powder, which crystallises from an ethereal solution in flattened orange prisms, which melt at 83—84°, forming a red liquid; at 87° the latter decomposes. On analysis, 0·1068 grm. gave 0·1618 grm. AgCl. Cl = 37·45.

0·2004 grm. gave 25·4 c.c. of moist nitrogen at 14° and 766 m.m. N = 14·95. $C_6H_2ON_2Cl_2$ requires Cl = 37·57; and N = 14·86 per cent.

This substance is very readily soluble in all solvents except petroleum; when dissolved in hot water it rapidly decomposes, the yellow solution becoming brown and turbid. It dissolves in concentrated solutions of acids, forming a nearly colourless liquid, which becomes yellow on adding water. These acid solutions couple with alkaline solutions of β-naphthol. There is no doubt that this substance is an ortho- and not a para-diazophenol, as *p*-diazophenols can be easily re-crystallised from hot water, whilst the ortho-compounds are decomposed by hot water. Again, *p*-diazophenols are easily reduced to *p*-aminophenols, but the ortho-derivatives are not reduced in a simple manner (Böhmer, *Journ. Prakt. Chem.*, 1881 [2], vol. xxiv., p. 460).

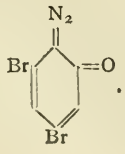
The amorphous yellow substances which are formed in the cases above described appear to be condensation products. The *o*-diazophenol which is produced has the para- and one ortho-position unoccupied, and being formed in the presence of a diazonium salt and sodium acetate or bicarbonate, is under conditions which are very favourable to the production of hydroxyazo-derivatives. A similar yellow powder is precipitated when sodium bicarbonate is added to a solution of the 3.5-dichloro-*o*-diazophenol. The yellow substances cannot be got to crystallise from any solvent; they decompose at 85°, and in a moist atmosphere slowly give off nitrogen; this is very noticeable when an attempt is made to estimate the nitrogen by Dumas' method. They do not dissolve in aqueous alkalis or acids. Cryoscopic determinations of the molecular weight in benzene show that, whether prepared by means of sodium acetate or bicarbonate, the molecule contains three benzeneazo-groups. There are three such compounds possible, formed by condensation either of (1) 2 mols. of *s*-trichlorobenzenediazonium salt with 1 mol. of the diazophenol ($(C_6H_2Cl_3.N_2)_2.C_6Cl_2\leqq^{N_2}_{O}$ has a mol. weight = 604; chloride = 46·8 per cent); or (2) of 1 mol. of the diazonium salt with 2 mols. of the diazophenol (mol. weight = 585·5; chlorine = 42·2 per cent); or (3) of 3 mols. of the diazophenol (mol. weight = 567; chlorine = 37·5 per cent). The material prepared by the use of sodium acetate has the highest percentage of chlorine, 44·7—44·9; its molecular weight was found to be 580—590; it is probably a mixture of (1) and (2). When bicarbonate is used, the yellow substance contains 41·4—43·7 per cent of chlorine; its molecular weight was found to be 560—580.

The Transformation of s-*Tribromobenzenediazonium Hydroxide.*

The transformation of *s*-tribromobenzenediazonium hydroxide resembles in its main features that of the *s*-trichloro-compound. *s*-Tribromobenzenediazonium nitrate, when first prepared, is pure white, although Silberstein (*Journ. Prakt. Chem.*, 1883 [2], vol. xxvii., p. 113) has described it as yellow. On keeping, it gradually acquires a yellow colour. Solutions both of the nitrate and the hydrogen sulphate become yellow, and bromine can be detected in the liquid. When either sodium hydrogen carbonate or sodium acetate is added to solutions of the salts, the decomposition is far more rapid. Thus in one experiment, in which sodium bicarbonate was added to a solution containing 1 grm. of the diazonium hydrogen sulphate, 0·31 grm. of silver bromide was obtained, whereas 0·508 grm. are required for the elimination of 1 atom of bromine.

In the presence of sodium acetate, the solutions of the diazonium salt rapidly become yellow and turbid. After twenty-four hours at 0°, a bulky and, at first glance, homogeneous precipitate had separated. In one experiment when 2 grms. of the sulphate were used, 0·58 grm. of silver bromide was obtained from the filtrate from the yellow precipitate. Careful examination of the yellow precipitate showed that it consisted of crystals completely covered and matted together by an amorphous yellow powder. These two substances could not be separated by crystallisation from any solvent. It was, however, found possible to obtain the crystals free from the powder by frequently shaking up the solid with water and decanting the supernatant liquor before the light powder had had time to settle.

3.5-*Dibromo*-o-*diazophenol* (3.5-*dibromo*-o-*diazoquinone*),



—The crystals just mentioned are the 3.5-dibromo-*o*-diazophenol in a state of purity. They are long slender transparent prisms of a fine orange colour, which explode when heated at 140°.

0·1894 grm. gave 0·2564 grm. AgBr. Br = 57·6.

(Two cryoscopic determinations of the molecular weight in benzene solution gave the values 278·9 and 281·6).

$C_6H_2ON_2Br_2$ requires Br = 57·53 per cent, and a molecular weight of 278.

The compound is very soluble in chloroform, benzene, ether, and glacial acetic acid, and in boiling alcohol. It is moderately soluble in boiling water, and very slightly so in cold water or petroleum. Treatment with hot water or alcohol decomposes it. It dissolves in concentrated acids, forming a colourless solution, and is re-precipitated by addition of water. The solution in acid couples with alkaline solutions of β-naphthol. The hydrochloride is obtained in nearly colourless needles by passing dry hydrogen chloride into a dry ethereal solution. This substance is without doubt the ortho-diazophenol, and not the 3·5-dibromo-*p*-diazophenol, which has been prepared by Silberstein (*loc. cit.*), and which can be crystallised from hot water.

In the account given by Hantzsch of the experiments above referred to, it is stated that on adding sodium acetate to the solution of a *s*-tribromobenzenediazonium salt, the whole of the latter is gradually converted into *s*-tribromophenylnitrosamine, $C_6H_2Br_3.NH.NO$, of which analyses are given: it forms an amorphous yellow powder, decomposing at 85°. By passing hydrogen chloride into the ethereal solution, he obtained a hydrochloride of the nitrosamine, which is immediately decomposed by water, a property possessed by the hydrochloride of the diazophenol.

The amorphous yellow powder, obtained by the author, both by the action of sodium hydrogen carbonate on the *s*-tribromobenzenediazonium salts, and mixed with crystals of the diazophenol when sodium acetate is used, decomposes at 85—90° (compare Hantzsch, 85°). The yellow substance appears to be similar to those obtained from *s*-trichlorobenzenediazonium salts; but determinations of the molecular weight indicate that only two benzeneazo-groups have condensed. In this case, however, the yellow powder certainly contained some of the diazophenol, as on passing hydrogen chloride into an ethereal solution of the powder, a small quantity of the hydrochloride of the last mentioned substance separated.

(The investigation of these intramolecular changes is being continued. It has been found that a similar interchange of halogen for hydroxyl takes place very readily in solutions of chloro- and bromo-naphthalenediazonium salts, even in the presence of excess of acid. The author is of opinion that the observations of Gaess and Ammelburg (*Berichte*, 1894, vol. xxvii., p. 2211) that an aqueous solution of 1-nitro-2-naphthalenediazonium sulphate yields the 1:2-naphthalenediazo-oxide is an example of the type of transformation here considered).

The Detection of Chromic Acid by means of Peroxide of Hydrogen, in the presence of Vanadic Acid.—C. Reichard.—The blue reaction of peroxide of hydrogen with chromic acid is prevented by the presence of vanadic acid. This influence cannot be attributed to a simple peroxidation of the vanadic acid, since an excess of peroxide of hydrogen does not bring the colour back; it is comparable rather with the decomposing action of the peroxides on chloride of lime. The phenomenon can be observed up to one part of vanadate of ammonium in ten parts of bichromate of potassium; it is no longer observed in the presence of phosphate or arseniate of soda. The presence of molybdic or tungstic acids is also inimical to the reaction of the perchromic acid.—*Zeit. Anal. Chem.*, vol. xl., p. 577.

ON THE MATERIAL OF CERTAIN CYPRIOTE CYLINDER-SEALS.

By Professor A. H. CHURCH, M.A., D.Sc., F.R.S., F.S.A.

It was in August, 1899, that my attention was first drawn by Dr. A. S. Murray, of the British Museum, to a seal-cylinder from Cyprus, which presented certain curious features. At first sight it appeared to be an engraved hæmatite, but on further examination the seemingly incuse designs which cover it revealed the characteristics of a casting from a mould in relief, while the material itself proved to be too soft and too brittle for hæmatite. Still the surface possessed the submetallic lustre of that substance, though rather violet in hue. The specific gravity of the cylinder was ascertained to be 5·36—a figure near to but rather higher than that of the compact black hæmatite usually employed for Babylonian and Egyptian objects of this class. A clue to the composition of this cylinder was furnished by the presence of a pale greenish deposit which filled up a part of the hollow axis. This was found to contain much calcium carbonate, along with distinct traces of calcium sulphate and of a compound of copper. The calcium carbonate being obviously extraneous it was possible that the cylinder itself might have been the source of the sulphur and of the copper which had been detected—might in fact consist of or contain a sulphide of copper. This was proved to be the case by an examination of a few scrapings which responded to the tests, physical as well as chemical, for cuprous sulphide (Cu_2S), a compound which occurs in nature as the mineral copper-glance or chalcocite. Some comparative experiments with scrapings of copper-glance, and scrapings of this Cypriote cylinder, showed that these two materials were virtually, if not actually, identical. They could not be distinguished under the microscope; they were alike in degree of fusibilty and in hardness (about 3). The specific gravity of the mineral ranges between 5·52 and 5·81, while the Cypriote cylinder under discussion was, it will be remembered, no higher than 5·36. But one expects to find a casting to be of lower density than the same material in a crystallised condition by reason of cavities and impurities in the former. And here I must refer to three other Cypriote cylinders of the same Mycenaean style, and obviously consisting of the same substance as the British Museum specimen. They are in the Ashmolean Museum at Oxford, and possess the specific gravities here recorded :—

Cylinder A (the largest)	5·504
Cylinder B (the next in size)	5·531
Cylinder C (the smallest)	5·313

These determinations, kindly made by Professor H. A. Miers, are in close accord with the figure I obtained from the British Museum example. I may add that I examined a few filings from Cylinder B, and found in them nothing save copper, sulphur, and traces of iron; indeed, in chemical as well as physical character, they correspond with cuprous sulphide. In this connection a fifth specimen should be cited. It is described in the "Catalogue of the Cyprus Museum" by J. L. Myres and Dr. M. Ohnefalsch-Richter as a cylindrical seal of the Bronze Age and of Mycenaean design. It is further stated that the design is "engraved on a black artificial paste resembling hæmatite," and that the material had been analysed by Dr. Weeren, of the Technological High School at Charlottenberg. I wrote to Dr. Weeren on the 19th of December, 1899, for details of his analysis, but have received no reply to my letter of inquiry.

The question now suggests itself, "Whence did the Mycenaean craftsman obtain his supply of cuprous sulphide?" At first I imagined that he might have had access to the mineral copper-glance, and have made a casting in a clay mould from this material after crushing and fusing it. But a more probable origin for this imitation of hæmatite was suggested to me by Mr. W. Gowland during my examination of a copper ingot, found in the year 1896 at Enkomi in Cyprus. This ingot (No. 113 in the British Museum Catalogue of Bronzes), which measures 2 feet 3½ inches in length, 16 inches in breadth, and 2 inches in thickness, and weighs 81 pounds 10 ounces, bears upon its lower face the Cypriote character—

On analysing the unaltered central portion of this ingot the following figures* were obtained :—

	Per cent.
Copper	98·05
Tin	nil
Lead	0·31
Bismuth	trace
Silver	trace
Zinc	0 05
Iron	trace
Sulphur	0·22

Now the side-light thrown upon the special inquiry in hand comes from the recognition of sulphur in this ingot, and from the detection of particles of a very impure cuprous sulphide amongst the drillings of metal handed to me for analysis. Clearly the ore from which this ancient ingot of copper had been reduced must have contained a fair quantity of unoxidised sulphides. Mr. Gowland thinks the metal was produced "by smelting *surface* ores consisting of carbonates and oxides mixed with some sulphide." He further remarks, "whenever a certain amount of undecomposed sulphides was present, the products of direct smelting would be copper similar to the Cypriote ingot, and varying amounts of regulus resembling or identical with the material of the cylinders." Now this regulus, consisting mainly of cuprous sulphide but with some FeS, probably represented a product of the furnace intermediate between the "blue metal" and the "white metal" of the modern metallurgist. This then was, in all probability, the substance which, seen in its fused state, the Mycenaean artisan recognised as offering a superficial resemblance to polished hæmatite. It did more than present such resemblance, for it possessed almost the same density as the much harder ore of iron. Here, then, was the very material wanted for casting, by an easy process, these "shoddy" cylinders, as I may venture to call them. They were cheap and quickly-made imitations of laborious engraved work, executed upon comparatively hard hæmatite. I ought, perhaps, to add here that the bluish-black regulus, obtained as above mentioned, though essentially cuprous sulphide, is by no means of constant composition and density. It is, therefore, not to be expected that this group of Mycenaean cylinder-seals should present an absolute uniformity in chemical and physical properties.

A striking confirmation of the suggested origin of the material of these Cypriote cylinders is afforded by the occurrence on the largest of the Ashmolean examples of a very good representation of an ingot like the specimen from Enkomi which I have described in the present note.—*Proceedings of the Society of Antiquaries*, May 29, 1902.

Addition Products of Cyclohexane.—Léon Brunel.—The author prepares several new derivatives of cyclohexane, and examines their properties. Iodhydrine of orthocyclohexanediol, the iodhydrine ether oxides, the methylic ether oxide, the ethylic ether oxide, and orthochloroiodcyclohexane.—*Comptes Rendus*, cxxxv., No. 23.

* The amount available for analysis was 6 grms. only. The two determinations of copper which were made differed by 0·10 per cent; the mean is inserted in the table of results. I am indebted to Mr. F. W. Harbord for all the results, save the percentage of sulphur; this is probably over-stated.

ON THE GRAVIMETRIC ESTIMATION OF TELLURIUM.

By R. W. EMERSON MacIVOR, F.I.C., &c.

In the methods for gravimetrically estimating Te ordinarily given in the analytical text-books, the substance is thrown out of solution in the elementary state by sulphur dioxide, or other reducing agent, and weighed in that form, or, after treatment with nitric acid and subsequent heating to fusion, as TeO_2.

The use of SO_2 as a precipitant in the quantitative determination of this element was first proposed by Berzelius, and the modification of the great chemist's process, recommended by Fresenius ("Chemical Analysis," vol. ii., p. 419, seventh edition), consists in adding to the tellurous HCl solution a strong aqueous solution of SO_2, and allowing the mixture to remain a few days in a warm place "to ensure complete precipitation." Now, it was shown by some of the older chemists, and in later years by Schrœtter, Brauner, Norris, Fay, Crane, and Frerichs, that it is not possible to precipitate all the tellurium from a strongly acid solution by SO_2 only. Moreover, Brauner (*Journ. Chem. Soc.*, vol. lv., p. 392) points out that part of the precipitated element undergoes oxidation in the acid liquid, becoming converted into $TeCl_4$, in which form it remains in solution. Crane suggests (*Am. Chem. Journ.*, xxiii., p. 408—425) that the main cause of the incompleteness of the action is the very rapid increase of the ratio of the acids to the unprecipitated tellurium in solution, two-thirds of this being due to HCl set free, and one-third H_2SO_4 formed, and that if these could be removed the reduction would go on to the end. So far as the HCl is concerned, it could be got rid of by simple evaporation, but then the continuous increase of the H_2SO_4 would soon again interrupt the reaction. By the careful use of KHO or NaHO this increase of acidity might, of course, be kept under control, but Whitehead, in proposing the acid sodium sulphite as an efficient precipitating agent solved the difficulty once and for all. It is true that this salt does not completely remove all the tellurium from solution in the cold, but if not used in great excess and the mixed solutions be raised to boiling point, towards the end of the action the precipitation is perfect, and the tellurium obtained in a state of aggregation favourable to easy filtration—an important consideration when the liability of the precipitate to undergo oxidation is borne in mind. The solution of sulphite should be moderately concentrated, and the quantity added to the tellurous solution sufficient only to just neutralise the acids present and formed in the reaction. On thoroughly agitating the solutions together, and then allowing the mixture to stand in a warm place, the precipitate will be found to form and settle evenly. It may be found advantageous to decant or filter the liquid from this precipitate before heating it to boiling point to obtain the last portion of tellurium. However this may be done every precaution must be taken to guard against the access of air to the wet precipitate. It will be noticed that the precipitate brought down by boiling is lighter in colour than the other formed in the cold or in mere warmth, but chemically the two are identical.

The completeness of the action of acid sodium sulphite on solutions of tellurium has been proved by Crane in a remarkable manner. An HCl solution containing only 0·00000214 grm. Te per c.c. gave a distinct reaction! "An effective surface of about one-half a square centimetre of white filter-paper was used to collect the precipitate, and on this the layer of black tellurium was plainly visible." In a still weaker solution the presence of the element was discernible, but "it appears probable that this limit is due simply to the fact that we have here nearly reached the physiological limit of seeing black on white."

The process recently devised by G. Frerichs (*Journ. Prakt. Chim.*, lxvi. [17], 261—262) is based on the fact that the simultaneous presence of HI and SO_2 causes the immediate and complete separation of tellurium from tellurous solutions even in the cold. To the solution in HCl of about 0·3 grm. of TeO_2 diluted to 100 c.c. with water, one to two grms. KI are added, and the whole heated to boiling; about 50 c.c. of an aqueous solution of SO_2 is next added, and, after settling, the precipitate is collected on a tared filter, first washed with water containing some SO_2, and finally with alcohol and ether. In practical working I can confirm all Frerichs has said for his process: it is rapid, the precipitate obtained filters easily, and can be quickly washed.

Crane suggests the use of metallic magnesium as a perfect precipitant for tellurium from hydrochloric acid solution. It is essential that the quantity of acid present should be as small as possible, and that a slight excess of magnesium should be employed. This latter may be oxidised by vigorous boiling and the resulting $Mg(OH)_2$ dissolved by the addition of acetic acid. Crane is of opinion that the tellurium precipitated by this method is not so prone to oxidation as that obtained by other processes. On this point, however, I am not prepared to say anything, but two trials of the process made in my laboratory satisfied me as to the reliability of the new process; the tellurium came quickly out of solution, and "left not a trace behind."

The rapidity with which tellurium precipitates undergo oxidation forms the main objection to the substance being weighed in the elementary form. We have seen that the process takes place with part of the substance thrown out of strongly acid solution by SO_2, and that that part remains afterwards in the liquid in the state of tetrachloride. During the operations of washing and drying the absorption of oxygen may be very considerable; hence these should be carried out as expeditiously as possible, and the precipitates should be kept as well covered with water as practicable to exclude air. It has been estimated by Norris and Fay (*Am. Chem. Journ.*, xx., p. 278) that under ordinarily careful conditions of working the precipitated tellurium increases in weight about 0·5 per cent owing to oxidation, and that this increase is balanced by the quantity of the element oxidised and left behind as $TeCl_4$ in the strongly acid solution in which the precipitate was formed by SO_2. In this case "the two sources of error" tend to neutralise each other, and the result obtained by estimating tellurium as Te by SO_2 precipitation may be taken as approximately true. However, the chemists last named are of opinion that "of the two gravimetric methods, weighing as TeO_2 and in the elementary state, the former alone is accurate." Brauner considers the results obtained by weighing tellurium precipitates quite unreliable, but at the same time points out that in the TeO_2 method the nitric acid is not entirely driven off before part of the dioxide is volatilised. This latter fact notwithstanding, chemists generally agree with the view expressed by the American chemists.

I hope soon to be in a position to put forward in the columns of this journal a really reliable gravimetric way of estimating tellurium. My results to date are certainly promising, but the continuity of my work is at present much interfered with, or perhaps an account of the new process would have formed part of the present communication.

Annuaire du Bureau des Longitudes.—The firm of Gauthier-Villars (55, Quai des Grands-Augustins, Paris) have just published their usual annual volume, the *Annuaire du Bureau des Longitudes* for 1903. It forms a compact volume in 16mo. of about 850 pages with figures, and costs post paid 1fr. 85c. It contains a fund of information indispensable to the man of science. Among the articles in this year's volume we may specially draw attention to that by M. R. Radau "On Shooting Stars and Comets," that of M. J. Janssen "On Science and Poetry," and to the discourses delivered at the funeral obsequies of MM. Faye and Cornu.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, December 17th, 1902.

Prof. J. EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Edwin Bayles Atkinson, Scarthe House, Great Grimsby; William Bowen Cleveden, Woodend Road, Erdington; R. C. Farmer, M.Sc., Ph.D., 154, Eglinton Road, Woolwich, S.E.; Frederic Herbert Lees, 256, Park Road, Crouch End, N.; A. H. Scholefield, B.A., B.Sc., 4, Hartley Terrace, Wolverhampton; Charles Tilburn, 31, Hardy Street, South Yarra, Melbourne; Andrew Young, M.A., B.Sc., 1, Avenue Terrace, Cape Town.

The following certificates were authorised by the Council under By-law I. (3):—K. Bhaduri, M.A., Professor, Canning College, Lucknow; George Montagu Prichard, Ramtek, Nagpur, C.P., India.

Of the following papers, those marked * were read:—

*180. "*A Reagent for the Identification of Carbamide and of certain other Nitrogen Compounds.*" By H. J. H. FENTON.

In previous communications to the Society (Fenton and Gostling, *Trans.*, 1899, lxxvii., 423; 1901, lxxxi., 807), various derivatives of methylfurfural have been described which are obtained from ketohexoses, or substances which produce these on hydrolysis, and from cellulose. Amongst these derivatives, a crystalline condensation product was mentioned having the formula $C_{11}H_8O_4$, the constitution of which is still under investigation; the evidence obtained so far indicates that it is either methylfuril, $C_4H_3O{\cdot}CO{\cdot}CO{\cdot}C_4H_2O{\cdot}CH_3$, or the ketone-aldehyde, $CHO{\cdot}C_4H_2O{\cdot}CO{\cdot}C_4H_2O{\cdot}CH_3$. The method of obtaining this substance has been considerably improved, so that it is now easy to prepare it in quantity. If a small quantity of this product be mixed with urea and the mixture treated with a trace of phosphorus oxychloride, acetyl chloride, or dry hydrogen chloride—dissolved in any appropriate solvent—a very brilliant blue colour is obtained. The reaction is one of extreme delicacy, 0·1 milligrm. of urea giving a strongly marked colour, and with care it is quite easy to detect 0·01 milligrm. or less.

This effect is due to a colourless base of which the salts have a blue colour. The intensity of the colour of these salts in aqueous solution varies markedly with the nature and concentration of the acid.

The production of a blue colour in the manner here described is characteristic of carbamide and of monosubstituted carbamides, $NH_2{\cdot}CO{\cdot}NHR$, in which the substituting radicle is an alkyl group or one of a similar character; acidyl substituted carbamides give no such reaction. Urethane gives a similar reaction, but the colour is red by transmitted light.

This compound also reacts with primary amines in acetic acid solution to give very brilliant green compounds; this change is produced at once on simply mixing the solutions without any condensing agent, and appears to be quite characteristic of primary amines.

DISCUSSION.

Mr. C. E. GROVES asked whether oxalic acid behaved like sulphuric and hydrochloric acids.

Mr. FENTON replied that the base gave a blue colour with oxalic acid also, the intensity of the colour being greater than that produced with acetic acid, but less than that with hydrochloric acid.

*181. "*The Rate of Decomposition of Diazo-compounds. Part II. Diazo-compounds of the Naphthalene Series.*" By J. C. CAIN and F. NICOLL.

The authors have extended their researches on the decomposition of diazo-salts (*Trans.*, 1902, lxxxi., 1412) to those of the naphthalene series, and find that the reaction is a unimolecular one in the case of the soluble diazo-salts prepared from the following amines:—

1. α Naphthylamine.
2. β-Naphthylamine.
3. Naphthylaminesulphonic acid .. .. $NH_2 : SO_3H = 1 : 8$.
4. Naphthylaminesulphonic acid .. .. $NH_2 : SO_3H = 2 : 6$.
5. Naphthylaminesulphonic acid .. .. $NH_2 : SO_3H = 2 : 7$.
6. Naphthylaminedisulphonic acid .. .. $NH_2 : SO_3H : SO_3H = 2 : 6 : 8$.
7. Naphthylaminedisulphonic acid .. .. $NH_2 : SO_3H : SO_3H = 2 : 3 : 6$.
8. Amidonaphtholdisulphonic acid .. .. $NH_2 : OH : SO_3H : SO_3H = 1 : 8 : 3 : 6$.

The unimolecular reaction, however, in the case of Nos. 1, 2, 4, 5, 7, 8, is hindered, after a considerable amount of decomposition has taken place, by the formation of azo-colours, which is clearly shown by the rapid diminution of the values of C, calculated according to the equation—

$$\frac{1}{t} \log \frac{A}{A - x} = C \text{ (a constant).}$$

The measurements were made at 60°, except in the case of No. 8, when the temperature was 80°. The diazo-salts are thus very stable.

In the case of the insoluble diazo-salts obtained from the following amines:—

9. Naphthylaminesulphonic acid, $NH_2 : SO_3H = 1 : 2$.
10. " " " $= 1 : 4$.
11. " " " $= 1 : 5$.
12. Amidonaphtholsulphonic acid, $NH_2 : OH : SO_3H = 2 : 8 : 6$.

the rate of decomposition is expressed by the equation $\frac{x}{t} = K$ (a constant), x being the observed volume of nitrogen evolved in the time t.

In each case, an azo-colour is formed towards the end of the reaction, shown again by the rapid diminution of the values of K.

These diazo-salts are very stable, the experiments being made at 70° or 80°.

In each case where an azo-colour is formed, the value of C or K is constant for a considerable period, showing that, although both naphtholsulphonic acid and diazo-salt are present, no combination takes place during this period.

The authors suggest that this interesting fact may be explained by assuming that hydrolytic dissociation of the diazo-salt is necessary before combination takes place; in the above experiments, the diazo-salt is not dissociated (especially in the presence of the free mineral acid, which has a retarding effect on the formation of an azo-colour) until its concentration becomes considerably less. When this point is reached, the formation of an azo-colour can proceed.

*182. "*State of Carbon Dioxide in Aqueous Solution.*" By J. WALKER.

The author gave a proof from the law of mass-action that carbonic acid (and similar substances) in aqueous solution must obey Ostwald's dilution law, independently of the proportions of the anhydrous and hydrated forms contained in the solution. The conclusion formerly drawn (Walker and Cormack, *Trans.*, 1900, lxxvii., 8), that the carbon dioxide in solution is probably hydrated to the extent of 20 per cent, must therefore be rejected.

*183. "*Qualitative Separation of Arsenic, Antimony, and Tin.*" By J. WALKER.

When a solution of the sodium thio-salts of arsenic, antimony, and tin is boiled with sodium peroxide, these

salts are converted into sodium arsenate, antimonate, and stannate respectively. Any mercury which may have been dissolved from the copper group on warming with sodium hydroxide, is, by this treatment, re-precipitated as sulphide. The tin may be separated from the arsenic and antimony by boiling with excess of ammonium chloride, which precipitates stannic hydroxide, leaving the antimony and arsenic in solution. On addition of excess of acid, these may be separated by means of sulphuretted hydrogen in the cold, the antimony being at once precipitated as sulphide, whilst the arsenic remains dissolved.

Discussion.

Dr. F. M. Perkin remarked that when stannous sulphide does not dissolve in caustic alkali, the addition of a little sodium or hydrogen peroxide enables it to do so. The peroxide seems to exert very little, if any, oxidising action upon the sulphides of the copper group, hence there is no objection to warming the mixed sulphides of these two groups with caustic alkali and sodium peroxide, and so obviating the use of ammonium sulphide.

*184. "*The Hydrates and Solubility of Barium Acetate.*" By J. Walker and W. A. Fyffe.

The authors have been unable to confirm the observations of Krasnicki (*Monatshefte*, 1887, viii., 601), who stated that the solubility of barium acetate between 0° and 80° could be represented by a single curve concave to the temperature axis. On the contrary they find that the solubility is expressed by three curves (for the trihydrate, monohydrate, and anhydrous salt, respectively), which are all convex to the temperature axis. The curve for the monohydrate exhibits a minimum at 30°, and that for the anhydrous salt a minimum at 75°.

The solubility and special dilatometric experiments showed the inversion temperature for—

$$Ba(C_2H_3O_2)_2,3H_2O \rightleftarrows Ba(C_2H_3O_2)_2,H_2O + 2H_2O$$

to be 24·7°; that for—

$$Ba(C_2H_3O_2)_2,H_2O \rightleftarrows Ba(C_2H_3O_2)_2 + H_2O$$

being 41°.

Discussion.

Professor Tilden expressed the belief that revision of many of the accepted data in regard to solubility was urgently required, and hoped that Professor Walker would continue his work in this direction. Published estimations of solubility of many metallic salts at temperatures above the boiling-point of water were absolutely valueless, inasmuch as evident chemical change sets in and basic salts are visibly deposited.

*185. "Cis- *and* trans-*αβ-Dimethylglutaric Acid and the Separation of the* cis- *and* trans-*forms of Substituted Glutaric Acids.*" By J. F. Thorpe and W. J. Young.

The αβ-dimethylglutaric acids are best prepared by the condensation of ethyl β-methylacrylate with ethyl sodiocyanacetate and subsequent treatment of the sodium derivative formed with methyl iodide.

Ethyl α-cyano-αβ-dimethylglutarate,—

$$CO_2Et\cdot C(CN)(CH_3)\cdot CH(CH_3)\cdot CH_2\cdot CO_2Et,$$

is a colourless oil which boils at 185° (20 m.m.), which, with cold methyl alcoholic potash, yields the *potassium* salt. *α-Cyano-αβ-dimethylglutaric acid* is a white solid which separates from ether and light petroleum in microscopic needles melting at 132—133°.

When this substance is heated with concentrated hydrochloric acid, it is in part converted into *αβ-dimethylglutarimide*,—

$$CH_3\cdot CH\!<\!\begin{matrix}CH(CH_3)\cdot CO\\ CH_2 \text{ —— } CO\end{matrix}\!>\!NH,$$

which crystallises from water in long needles melting at 113°, and in part into trans-*αβ-dimethylglutaric acid*, which appears to be a liquid at the ordinary temperature.

The imide, on hydrolysis with sulphuric acid, yields *cis-αβ-dimethylglutaric acid*, which crystallises from concentrated hydrochloric acid in needles melting at 87°.

The *trans*-acid is unacted upon by acetyl chloride, but when boiled with acetic anhydride or when slowly distilled under atmospheric pressure it is converted into the *anhydride* of the *cis*-acid, which may also be prepared by the action of acetyl chloride on the *cis*-acid. It is a liquid boiling at 255° (765 m.m.). The *anilic acid* separates from dilute alcohol in lustrous plates melting at 149°. The *cis*-acid, on heating in a sealed tube with concentrated hydrochloric acid, is converted into a mixture of the *cis*- and *trans*-acids.

The authors described the preparation of *αβ-dimethylpropanetricarboxylic acid*,—

$$(CO_2H)_2\cdot C(CH_3)\cdot CH(CH_3)\cdot CH_2\cdot CO_2H,$$

which crystallises from dilute hydrochloric acid in white needles melting with evolution of carbon dioxide at 165°. When heated to 200°, this acid is converted into a mixture of *cis*- and *trans*-αβ-dimethylglutaric acids.

The *cis*- and *trans*-forms of substituted glutaric acids may be separated by converting the mixed acids into their ammonium salts, and heating them in a sealed tube at 160° for four hours. In this way, the ammonium salt of the *cis*-acid is converted into the imide, which, on hydrolysis with sulphuric acid, yields the *cis*-acid, whilst the *trans*-ammonium salt remains unchanged. The imide and ammonium salt are separated by means of ether.

The separation of *cis*- and *trans-αα'*-dimethylglutaric acids, of *cis*- and *trans-α*-methyl-*β-iso*propylglutaric acid, and of *cis*- and *trans-αα'ββ*-tetramethylglutaric acids have been thus effected.

*186. "*Constitution of Metallic Cyanides.*" By J. E. Marsh.

Volhard (*Annalen*, 1890, cclix., 378) has shown that potassium cyanide is oxidised by potassium permanganate to potassium cyanate. Other cyanides are similarly oxidised. Ammonium cyanide is thus converted directly into urea. There are two exceptions among metallic cyanides; silver and mercury cyanides are not oxidised by potassium permanganate. This reaction brings the cyanides of silver and mercury into relationship with the nitriles, which are also unattacked. On the other hand, the other cyanides are brought into association with the readily oxidisable carbamines. The author thinks that silver cyanide should be represented as Ag·C⋮N, and potassium cyanide as K·N:C.

Discussion.

Dr. Wade said he thought it was unsafe to infer a difference in the constitution of potassium and silver cyanides from the difference in behaviour of these salts towards oxidising agents. The potassium salt is freely ionised in aqueous solution, whilst the silver salt is insoluble and not appreciably ionisable; the stability of the latter towards oxidising agents is thus explained without having recourse to the hypothesis of a nitrilic constitution. Potassium cyanide resembles the alkyl *iso*cyanides in readily undergoing oxidation, as in most other respects (*Trans.*, 1902, lxxxi., 1606), but its ready ionisability in in this case destroys the parallel; the products of the oxidation of the undissociated alkyl *iso*-cyanides are complex and not comparable with the alkali cyanates, which are formed by the oxidation of *iso*-cyanogen ions.

*187. "*Auto-reduction of Mercury and Silver Cyanides.*" By J. E. Marsh and R. de J. F. Struthers.

On the hypothesis that silver and mercury cyanides have the nitrile constitution, attempts have been made to bring about the hydrolysis of the (CN) group, if possible without breaking off the metal. In all the reactions tried in which the (CN) group is hydrolysed, it is broken off from the metal.

When mercuric cyanide is heated with a strong solution of potassium hydroxide, the salt is reduced to metallic mercury. The same reduction is brought about by boiling the salt with a solution of sodium or potassium hydroxide or ethylate in excess of alcohol. Cyanide and cyanate of the alkali are formed. The alkali cyanide

formed protects the mercury salt from reduction, so that only half of the mercury is reduced. If potassium cyanide be previously mixed with the mercury salt, no reduction occurs. An intermediate product is being further investigated. Silver cyanide is also reduced in the same way.

When mercury cyanide is heated with from sixty to eighty times its weight of a mixture of equal volumes of sulphuric acid and water, hydrogen cyanide, and carbon dioxide are evolved at about 130°, and the whole mass sets to a jelly, from which mercurous sulphate is obtained on filtration; ammonium sulphate is also formed. The decomposition of the cyanide may be represented thus:— $2HgC_2N_2+2H_2O+H_2SO_4=Hg_2SO_4+3HCN+CO_2+NH_3$. The decomposition of the cyanide is, however, not complete, and if the temperature is allowed to rise above 140°, whether the precipitate is previously removed or not, a further reduction takes place, with separation of metallic mercury. If mercury cyanide is heated with water in a sealed tube, the salt is completely decomposed, giving mercury, carbon monoxide, and ammonium carbonate. The reaction begins below 230°, and may be thus expressed— $HgC_2N_2+4H_2O=Hg+CO+(NH_4)_2CO_3$. No oxalic acid was obtained, but it was found that ammonium oxalate, under the same conditions, breaks up into carbon monoxide and ammonium carbonate. Silver cyanide is also reduced to metallic silver when heated with water.

188. "*Note on the Action of Acids on Cellulose.*" By Miss M. Gostling, B.Sc.

In previous communications it has been shown that all forms of cellulose, when heated to about 80° with a saturated solution of hydrochloric or hydrobromic acid in chloroform or carbon tetrachloride, yield ω-chlorobromomethylfurfural, and that dextrose (which could be extracted with water after separation of the methyl furfural derivative) was formed at the same time. Hence the presence of a ketose as well as an aldose nucleus in cellulose was conclusively proved.

In every case, about 40 per cent of a black residue which retained the fibrous structure of the original cellulose was left after the action of the acids.

In the hope of throwing further light on the constitution of cellulose, the nature of this residue was investigated, and it was prepared free from any of the original cellulose by repeated treatment with hydrochloric acid until no more of the furfural derivative was formed.

Chlorine acted very slowly on this black residue, giving yellow derivatives containing from 25·7 to 34·35 per cent of chlorine.

The action of bromine was similar.

Nitric acid (sp. gr. 1·2) and alkaline permanganate oxidise it to oxalic acid.

The original black residue is quite insoluble in alkalis, water, alcohol, ether, and other organic solvents.

The composition and general character of this residue is therefore closely allied to the substances known as artificial humus, obtained by Conrad and Guthzeit and by Sestini by the action of dilute acids on sugars. It corresponds most nearly with sacculmin (prepared by Sestini by boiling cane-sugar with dilute sulphuric acid), which was a black, amorphous mass, insoluble in potash solution, giving with chlorine yellow chlorine compounds. Sestini gives to sacculmin the formula $C_{44}H_{38}O_{15}$ (C = 65·5; H = 4·8 per cent), a slightly higher percentage of carbon and hydrogen than that in the black residue from cellulose (found C = 62·31 to 62·70; H = 3·64 to 4·29).

189. "*Nitrotartaric Acid and some of its Ethereal Salts.*" By P. F. Frankland, H. L. Heathcote, B.Sc., and Miss H. Hartle, B.Sc.

The announcement in the current number (December 6th) of the *Berichte* that a paper is to be communicated to the Berlin Society on December 8th by Professor P. Walden on the nitromalic and nitrotartaric esters, compels the authors to publish without delay the results of work on which they have been engaged during the past four years.

Their investigation has included the preparation and characterisation of the following compounds:—Dinitrotartaric acid, dimethyl dinitrotartarate, diethyl dinitrotartrate, dimethyl mononitrotartrte, and diethyl mononitrotartrate. Of these, dinitrotartaric acid was first obtained by Reinsch (*Jahrb.*, 1849, 329) and Dessaignes (*Jahrb.*, 1852, 475), whilst Henry (*Ber.*, 1870, iii., 530) professes to have prepared diethyl dinitrotartrate; the other compounds are, as far as the authors are aware, described for the first time. The only reference to the optical properties which they have been able to discover in chemical literature is the statement by Dessaignes that Chautard had found dinitrotartaric acid to be optically active and dinitroracemic acid inactive. With regard to diethyl dinitrotartrate, the authors are of opinion that Henry must have been dealing with the mononitrotartrate, inasmuch as he gives no analysis, and the melting-point 45—46°, which he records is very different from that which the authors have found, 27°, for the dinitro-, but very similar to that, 47°, which they have found for the mononitro-compound.

The authors have determined the optical activity of all these compounds dissolved in methyl and in ethyl alcohol, and, except in the case of dinitrotartaric acid, in benzene also.

The influence on the optical activity of the introduction of the nitro-group into the molecules concerned was also discussed.

190. "*The Nitration of Diethyl Monobenzoyl- and Mono-p-toluyl-tartrates.*" By P. F. Frankland, H. L. Heathcote, B.Sc., and C. J. Green, M.Sc.

For the reasons given in the preceding abstract, the authors wish to communicate the results which they have obtained in this investigation, which was also commenced four years ago.

Diethyl mono-benzoyltartrate and mono-*p*-toluyltartrate were nitrated in the hope of obtaining their mono-nitrates. In both cases, however, only compounds in which the nitro-group had entered the benzene ring were obtained. By hydrolysis it was shown that the *m*-nitrobenzoyl group was present in the one case, and the nitro-*p*-toluyl group ($CH_3:NO_2:CO = 1:2:4$) in the other.

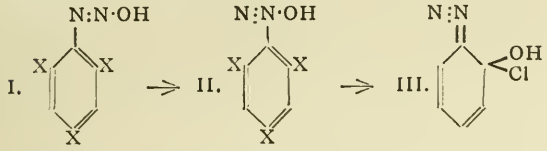
The rotation of these compounds was determined in solution in ethyl alcohol, ethyl acetate, benzene, pyridine, and chloroform. Their optical activity was enormously influenced by the solvent; thus the mono-*m*-nitrobenzoyl compound was inactive in benzene, although it exhibited considerable activity in the other solvents employed.

191. "*Interchange of Halogen for Hydroxyl in Chloro- and Bromonaphthalenediazonium Hydroxides.*" (Preliminary notice.) By K. J. P. Orton.

It has recently been shown by the author that *s*-trichloro- and *s*-tribromo-benzenediazonium compounds undergo a remarkable isomeric change under certain conditions. If aqueous solutions of such salts as the diazonium nitrate or hydrogen sulphate are kept for a short time, the presence of chloride may soon be recognised by means of silver nitrate; at the same time, the solution becomes yellow, owing to the formation of the *o*-diazophenol (*o*-diazoquinone). The salts of a weak acid, such as the acetate, undergo the same change far more rapidly.

These facts lead to the conclusion that this change is a transformation of the diazonium hydroxide, $C_6H_2X_3{\cdot}N(OH){:}N$, formed by hydrolytic dissociation; the weaker the acid, the larger would be the proportion of the diazonium hydroxide present at any one time, and consequently the more rapid the change. Moreover, the presence of a sufficient excess of acid stops the change. Treatment with excess of alkali (hydroxide or carbonate), on the other hand, does not effect the elimination of halogen, but merely converts the diazonium compound, $C_6H_2X_3{\cdot}N(A){:}N$, into the diazotate (*iso*- or *anti*-diazotate), $C_6H_2X_3{\cdot}N{:}N{\cdot}OM'$. If dilute acid is cautiously added to a solution of the di-

azotate, halogen is also eliminated. On treatment with acid, the alkali diazotate should first of all yield the corresponding acid, the diazohydrate, $C_6H_2X_3{\cdot}N{:}N{\cdot}OH$, but as is well known, these acids appear to change immediately into neutral substances, probably primary nitrosoamines. In the reaction here described, it would seem that the diazo-hydrate (I.) is either transformed into the diazonium hydroxide (II.) (or its ions), and then into a complex (III.) of the quinone type, or else directly into this complex; from this quinonoid



compound, hydrogen chloride (or bromide) is eliminated, and a diazoquinone produced, or the halogen wanders to the nitrogen, a phenol diazonium salt being formed.

As the tendency to pass into the quinone type seems to be greater in the naphthalene series than in the benzene series, it would be expected that this transformation would take place with greater readiness in the case of naphthalenediazonium compounds. Meldola and Streatfeild (*Trans.*, 1895, lxvii., 908), who first observed this type of replacement of bromine by hydroxyl, have obtained 4-bromo-2-diazo-1-naphthol by treatment of 1:-4-dibromo-2-naphthylamine, dissolved in acetic acid, with sodium nitrite, and subsequent boiling of the mixture with water. The author has studied the transformation of chloro- and bromo-naphthalenediazonium oxides, the solid salts of which have not hitherto been prepared.

1-Chloro-2-naphthalenediazonium hydrogen sulphate, $C_{10}H_6Cl{\cdot}N(SO_4H){:}N$, prepared from 1-chloro-2-napthylamine, can be obtained (but with considerable difficulty) in the form of colourless needles, very soluble in water and acetic acid and moderately so in methyl alcohol. Exposed to the air, the crystals become yellow in a few minutes. The aqueous solution of the hydrogen sulphate, which is of course strongly acid, very rapidly becomes yellow and turbid. In the presence of sodium acetate, the change was complete in a few hours, and 2-diazo-1-naphthol (2-diazo-1-naphthoquinone), $O{:}C_{10}H_6{:}N_2$, had separated in long, slender, golden-yellow needles (m. p. 76—77°); at the same time, a small quantity of an amorphous, yellow solid containing chlorine was formed; it is probably an azo-condensation product. The chloride formed in the solution fell but little short of that contained in the diazonium salt. On passing dry hydrogen chloride into an ethereal solution of the diazonaphthol, a nearly colourless, crystalline *hydrochloride* is obtained.

2:4-Dibromo-1-naphthalenediazonium hydrogen sulphate, $C_{10}H_5Br_2{\cdot}N(SO_4H){:}N$, crystallises in colourless needles which are considerably more stable than the β-naphthalene derivative just described (compare Knoevenagel, *Ber.*, 1895, xxviii., 2052). The aqueous solution of this salt rapidly becomes yellow, and after a short time begins to deposit the diazonaphthol in small rosettes of needles. In the presence of sodium acetate, the diazonium salt is completely decomposed in twenty-four hours, one atomic proportion of bromine being found in the solution. *4-Bromo-1-diazo-2 naphthol* (*4-bromo-1-diazo-2-naphthoquinone*), $O{:}C_{10}H_5Br{:}N_2$, crystallises from dilute alcohol in rosettes of bright yellow needles, which melt and decompose with evolution of gas at 132—133°; it yields a nearly colourless *hydrochloride*.

192. "*Purpurogallin.*" By A. G. Perkin and A. B. Steven.

The discovery of Nietzki and Steinmann (*Ber.*, 1887, xx., 1277) that purpurogallin, on distillation with zinc dust, yields naphthalene has been confirmed. On methylation, purpurogallin gives a *trimethyl ether*, $C_{11}H_5O_2(OCH_3)_3$, orange-yellow needles, m. p. 174—177°, which forms a *monoacetyl* derivative, $C_{11}H_4O_2(OCH_3)_3{\cdot}C_2H_3O$, needles, m. p. 140—143°, and by the action of alcoholic potash at 170° yields a crystalline acid, m. p. 197—199°. The latter, on distillation, is converted into an anhydride, m. p. 164—166°. By digestion with 50 per cent potassium hydroxide solution, purpurogallin is converted into two isomeric compounds possessing almost identical reactions, to which the names *purpurogallone* and *iso-purpurogallone* have been given. The former, minute yellow needles, m. p. 260—262°, has probably the formula $C_{11}H_6O_5$, and gives the anhydroacetyl compound, $C_{11}H_2O_4(C_2H_3O)_2$, colourless, prismatic needles, m. p. 174—176°, whereas the latter, $C_{11}H_6O_5$, yellow needles melting above 300°, gives, with acetic anhydride, the compound $C_{11}H_2O_4(C_2H_3O)_2$, colourless, prismatic needles, m. p. 280—282°. It is probable that both compounds contain a carboxyl group.

193. "*Note on the Destructive Distillation of Ethyl Gallate.*" By A. G. Perkin.

According to Schiff (*Annalen*, 1872, clxiii., 217), on distillation, ethyl gallate gives pyrogallol and ethyl alcohol. This is so, but at the same time, towards the end of the operation, a considerable quantity of a red colouring matter sublimes, which has been identified as *rufigallic acid* (hexahydroxyanthraquinone) (found, C=55·14; H=2·63), by its acetyl derivative, $C_{14}H_2O_4(C_2H_3O)_6$ (found, C=55·78; H=3·85; $C_{14}H_8O_4$=55·09), m. p. 282—283° (not previously given), and by its dyeing properties. The yield was approximately 7 per cent, but considerable carbonisation occurs when this colouring matter is distilled. The reaction may be expressed as $2C_6H_2(OH)_3{\cdot}CO_2Et = C_{14}H_8O_8 + 2EtOH$. Gallic acid itself, on distillation, yields a small quantity of the same substance (acetyl compound, C=56·17; H=377), whilst protocatechuic acid and its ethyl salt give a trace of a colouring matter resembling rufiopin. β-Resorcylic acid does not give rise in this way to any anthraquinone derivative,

194. "*A Series of Double Chromates.*" By S. H. C. Briggs.

The author has found that freshly precipitated copper hydroxide or carbonate dissolves in one equivalent of chromic acid to give a clear solution in the presence of twenty or thirty equivalents of copper sulphate, or ten to fifteen equivalents of copper silicofluoride, although in the absence of these salts the dichromate and a precipitate of basic salt are produced.

A double salt, $(NH_4)_2Ni(CrO_4)_2{,}6H_2O$, was obtained by adding ammonium chromate to a solution of a nickel salt. This could be re-crystallised from water below 40°, although nickel chromate has never been obtained from aqueous solution, and ammonium chromate can only be re-crystallised from solutions containing ammonia. Attempts to prepare the potassium nickel chromate and double chromates of ammonium and copper, zinc, cadmium, and manganese were unsuccessful.

By the action of ammonia on the mother liquors from the preparation of $(NH_4)_2Ni(CrO_4)_2{,}6H_2O$ from the chloride, a double salt, $(NH_4)_2Ni(CrO_4)_2{\cdot}2NH_3$, was obtained, and corresponding copper, zinc, and cadmium compounds were formed by the action of ammonia on the dichromates. These double salts, on heating, lose water and ammonia, and undergo sudden decomposition between 200° and 300°, leaving a mixture of oxides.

Para-benzene-azobenzoic Aldehyde and its Derivatives.—P. Freundler and M. de Laborderie.—Since their original preparation of *p*-benzene-azobenzoic aldehyde the authors have discovered a method of preparing this aldehyde which avoids the separation of the two mixed symmetric acetals and the condensation of the nitroso-benzene with *p*-amino-benzoic aldehyde. This aldehyde being difficult to manipulate on account of its easy polymerisation, the authors try to substitute one of its immediate derivatives. *p*-Benzene-benzaldoxime, $C_6H_5N{=}NC_6H_4CH{=}NOH$, is described.—*C. R.*, No. 24.

NOTICES OF BOOKS.

The New Volumes of the Encyclopædia Britannica. The Seventh of the New Volumes, being Vol. XXXI. of the Complete Work. London: *The Times.* Edinburgh: Adam and Charles Black. 1902. Pp. 909.

The subjects included in this volume are those coming within the alphabetical headings MOS (Mosaic) and PRE (Prevasa).

The general standard of interest is well maintained in this volume, but the subjects of special scientific interest are fewer than in some of the earlier volumes.

The articles on "Motor Vehicles," by the Hon. C. S. Rolls and Professor H. S. Hele-Shaw, F.R.S., will be read with interest; of these two writers the former is well known as one of the foremost exponents of the practical side of the subject, while the last named is more closely allied with its theoretical aspect; in his recent Christmas lectures at the Royal Institution he took motor vehicles as one of his principal subjects.

To those mathematically inclined there are several articles worth attention, such as the "Laws of Motion," by W. H. Macaulay, and "Number," by G. B. Matthews, F.R.S. The series of articles on "Ordnance" by a number of distinguished writers, is of importance, and is fully illustrated. "Ore-dressing," by R. H. Richards, B.Sc., is of considerable interest to mining engineers and metallurgists; the author has divided his subject into three parts:—(1) The properties of minerals which render aid in their separation; (2) simple operations; and (3) operations combined to form processes or mills. With regard to properties, specific gravity is the most important in ore-dressing by settlement, either in air or water, but for hand-picking, colour, lustre, and fracture are of special value. Among the simple operations described and illustrated, the rock-breaker, the rolls, and the stamp mills are the principal, and after being treated in one or more of these, the crushed ore has to be concentrated; this operation can be done in a variety of manners, by buddles, jigs, vanners, &c.; these necessitate combined operations, and some of the more important of these mill schemes are described, such as those for zinc, lead, copper, tin, iron, gold, and asbestos ores, &c.

The "Oyster Industry" is one which has come prominently before us quite recently, owing to the unfortunate pollution of some oyster-beds by sewage; in the article dealing with this subject the writer gives a goodly number of statistics as to how many millions are sold, but no mention is made as to the very necessary precautions which should be taken in laying and stocking beds against their pollution by the sewage from neighbouring towns, discharged in the vicinity.

"Photography" is ably treated by Sir W. Abney and others, the subject being divided into three parts:—Scientific, apparatus, and pictorial. The "Phonograph," by J. G. M'Kendrick, is well written, and contains a number of interesting diagrams of vibrations or sound-waves of different languages, &c. Among other attractive articles, we may mention those on "Pneumatic Tools," "Oceanography," "Pathology," &c.

Physico-Chemical Tables; for the Use of Analysts, Physicists, Chemical Manufacturers, and Scientific Chemists. In Two Volumes, each complete in itself. Vol. I. *Chemical Engineering and Physical Chemistry.* By John Castell-Evans, F.I.C., F.C.S. London: Charles Griffin and Co., Ltd. 1902. Pp. 548.

This work has been designed to be of use to all engaged or interested in any branch of chemistry and metallurgy; it covers more ground than in any of the well-known "pocket-books," to which it is perhaps hardly fair to compare it, as it stands on a different footing to most of them. The author's first intention was to make two separate collections of tables, one for practical men and manufacturers, and the other for purely scientific investigators and college professors, but it was found to be impossible to make the division. Not only would there have been a great deal of overlapping, but there was also the thought that the practical man is rapidly finding that what was but recently a purely scientific method, is now a commercial and manufacturing process; in fact, the laboratory is invading and absorbing the works; in other words, our science is becoming more practical and our works more scientific. For such reasons it was decided to combine both kinds of tables in one work.

The tables in this volume are sixty-nine in number, and each one is divided into a number of sections. Most of them are original work, and have been calculated or re-calculated by the compiler.

Pages 11 to 19 form a descriptive list of the tables, with notes on the use and application of the most important ones. Part I. is on Mathematics, Part II. on Mechanics, and Part III. on Physics, &c.

As a general rule, the English nomenclature and terminology has been adopted, but in the case of the aromatic hydrocarbons the German termination, -ol, has been adopted, *e.g.*, benzol, toluol, instead of benzene, toluene.

On the completion of the second volume an index of trades and industries will be added, showing what tables will be of most service to those engaged therein. The book gives evidence of a large amount of careful and laborious work, and will be of great use to scientific and practical men alike.

Bacterial Treatment of Crude Sewage. Fourth Report. By Dr. Clowes, F.I.C., &c. London: P. S. King and Son. 1902. Pp. 150.

The experiments described in this report are those which have been carried out on crude London sewage in settling-tanks and coke-beds at Barking and Crossness. The whole of the raw, unsettled sewage of the metropolis was formerly allowed to flow into the Thames without any previous treatment. The result was that the stream became insupportably foul, partly from the sewage mud itself, and partly through putrid changes occurring in the sewage matter dissolved in the water. Some time ago the main source of the nuisance was removed by screening and settling, and, finally, it was decided to purify the effluent further before it entered the river.

These experiments have been going on for four years, on a large scale, and the results arrived at are of great importance and worthy of the most serious consideration.

By the method of working which has been finally adopted after constant improvements and extensions, the raw sewage, screened from the coarser matter only, is pumped continuously into a settling-tank, at such a rate that it remains in the tank for about six hours before flowing into the coke-beds. In this tank the sludge settles, and a considerable proportion, up to 50 per cent, disappears through bacterial action. By the subsequent coke-bed treatment, the effluent is rendered sufficiently pure to support the life of fish, and to insure it against undergoing any offensive change, even in summer. Some of the principal points established by this experimental work are, that the sludge which settles out is reduced very considerably by bacterial action; that the coke-bed does not choke, and its purifying power undergoes steady improvement for some time; that the "bacterial effluent" never becomes offensive, and that the use of chemicals is quite unnecessary under any circumstances when this method of treatment is adopted.

The bulk of the report consists of tabulated results of different kinds, more than three-quarters being particulars of the bacteria beds, &c., at various centres throughout the country, either in permanent installations or in experimental form. This information has been placed in two

main divisions, one dealing with the bacteria (or coke) beds, and the other with the septic tanks.

To Londoners, however, the two sections dealing with the work carried out at the northern and southern outfalls, situated respectively at Barking and Crossness, is the most interesting.

An examination of the figures given for the amount of oxygen absorbed from permanganate, gives the clearest idea of the purification effected. To summarise a few of the figures only, we find that at the northern outfall works, the crude sewage absorbed an average of 12·711 parts of oxygen per 100,000; the effluent from the primary coarse coke-bed 3·213 parts, and the final effluent from the secondary fine bed only 1·726, during the year 1900. In another table we note that the sewage supplied to a coke-bed absorbed 9·076 parts of oxygen per 100,000, the effluent from the chemically treated and sedimented sewage 7·671 parts, and the effluent from the coke-bed 1·214 parts per 100,000. In the second case every effluent was putrescible, while in the latter case it was never so.

Dr. Clowes recommends, as a result of his prolonged experiments, that the London sewage should be treated by this method without delay. Of course, it would have to be done gradually, and the beneficent results would not be very apparent for some years. But we cannot find, in this report, any definite statement as to the extent of the works necessary to treat London's daily sewage, and this must be of necessity very great. The daily water supply may be taken at 200,000,000 gallons, and practically the whole of this finds its way back into the river through the sewers, to say nothing of the additional water, due to the rainfall over London's 400 square miles. Without going into further figures it appears as if the area required for coke-beds would be prohibitory, while the settling-tanks to allow of six hours' sedimentation would have to be of enormous extent.

CORRESPONDENCE.

IODINE AND BROMINE.

To the Editor of the Chemical News.

Sir,—In the *Journal of the Society of Chemical Industry* for November 29th last, I find that Dr. F. Mollwo Perkin has published a method for detecting iodine and bromine by means of the hypochlorites and sulphide of carbon.

It may interest many of your numerous readers that this method was made known by me in 1867—that is, thirty-five years ago. My note was published in the *Comptes Rendus*, under the title:—"Sur une Réaction trés simple pour reconnaître l'Iode at la Brome dans une même Solution." In this note I showed that the hypochlorites isolated, firstly, all the iodine, and afterwards the bromine, the first substance giving the well-known purple tint to the sulphide of carbon, which was afterwards changed to brownish yellow, or yellowish brown, on continution of the reaction, as the bromine was set free, and the colour due to iodine disappeared. I was enabled by this reaction to put in evidence, in the cold, both bromine and iodine in the sea-water at Ostend.—I am, &c.,

T. Lamb Phipson, Ph.D.

Diffusion of Arsenic in Nature.—F. Garrigou.—The author uses Bunsen's flame method for the detection of traces of arsenic, with the aid of the spectroscope, microscope, and the ordinary reactions. He finds arsenic in all rocks, in all crystalline minerals, in metallic fibres, in mineral waters, in drinking waters, in vegetable ash, and in all animal organisms. He concludes, therefore, that arsenic is one of the most widely distributed of all the metalloids.—*Comptes Rendus*, cxxxv., No. 24.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

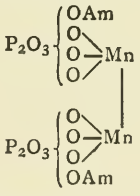
Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 24, December 15, 1902.

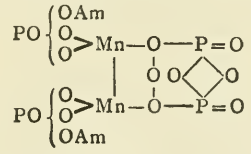
Aluminium Fluoride.—E. Baud.—Very little research has been done on the fluorine derivatives of aluminium since the work of Sainte-Claire Deville, and this is no doubt owing to the difficulty of analysing these compounds. The author prepares—(1) The hydrated fluoride of aluminium, and calculates its heat of formation; (2) the anhydrous fluoride, which is insoluble in all substances, even in concentrated hydrofluoric acid. In order to determine the heat of formation of this substance from known thermic constants, one essential number is missing—the heat of solution of the anhydrous fluoride or its heat of hydration, quantities impossible to measure with any degree of accuracy. Therefore his result, 498·98 cals., can only be considered as the nearest approximation.

Action of Boron Chloride on Ammonia Gas.—A. Joannis.—During the action of boron chloride on ammonia, the author finds that no gas is evolved, and it seems that the following action takes place:—Chloride of ammonium and boron amide being formed at $-23°$, $BoCl_3+15NH_3=3(NH_4Cl,3NH_3)+Bo(NH_2)_3$; and at 0°, $BoCl_3+6NH_3=3NH_4Cl+Bo(NH_2)_3$. This reaction is slow.

A Violet Ammoniacal Manganic Phosphate.—Ph. Barbier.—During the author's researches on the rose-coloured phosphate of Gmelin, he succeeded in preparing a new manganic phosphate of a much bluer and darker colour. He describes the preparation, and finds from analysis that it has the empirical formula $P_4O_{14}Mn_2,Am_2$, or the constitutional formula—



or it may be considered to be an ammoniaco-manganic diorthodimetaphosphate,—



Separation of the Alkalis from Manganese Peroxide.—H. Baubigny.—The author devises a simple method by which manganese peroxide may be separated from the alkalis and estimated quantitatively when in solution with these substances.

Oxybenzylphosphinic Acid.—C. Marie.—The author continues his researches on oxybenzylphosphinic acid, and prepares its silver salt, its methylic ether, and its benzoïl derivative.

A New Method of Chlorination of the Aromatic Carbides.—MM. Seyewetz and Biot.—Plumbico-ammoniacal chloride easily decomposes under the action of heat or reducing substances, giving lead chloride and ammonium chloride and chlorine. The authors employ this nascent chlorine to chlorinate the aromatic carbides, toluene, paraxylene, naphthalene, and anthracene.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, January 13th, at 5 o'clock, Professor Macfadyen delivers the first of a course of six lectures at the Royal Institution on the "Physiology of Digestion"; on Thursday, Mr. A. J. Evans begins a course of three lectures, at the same hour, on "Pre-Phœnician Writing in Crete, and its Bearing on the History of the Alphabet"; and on Saturday, at 3 o'clock, Sir Frederick Bridge delivers the first of three lectures on the "Bi-Centenary of Samuel Pepys, his Musical Contemporaries, Criticisms, and Compositions" (with musical illustrations). The Friday evening Discourse on January 16th will be delivered by Professor Dewar on "Low Temperature Investigations"; on January 23rd by Dr. Tempest Anderson on "Recent Volcanic Eruptions"; and on January 30th by Professor W. E. Dalby on "Vibration Problems in Engineering Science."

Cathodic Polarisation and the Formation of Alloys.—A. Coehn.—The author has examined the formation of the alloy of two metals, MM', by the electrolytic deposition of the metal M on a cathode formed of the metal M', supposed to be less oxidisable (more noble) than M. He observes that in this case the potential of discharge of the metallic ions is diminished even when the two metals M and M' are solid. When the metal M is mercury, the liquid condition of which facilitates the diffusion of the metal deposited in the mass of the cathode, the phenomenon aquires a special distinctness. The tendency of different metals to form amalgams corresponds with the lowering of their potential of discharge on contact with a mercurial cathode; it decreases on passing from one term to another of the following series:—Zinc, cadmium, silver, copper, iron. When the metal M is hydrogen, we observe that palladium alone gives a potential of discharge lower than the point of reversible decomposition; thus, this metal is the only one with which hydrogen forms an alloy. The examination of the curves of decomposition of a solution of potash in the presence of different cathodes, and notably of a mercurial cathode, shows that the second point of cathodic decomposition corresponds with a complex ion of which the formula is apparently KH_2. From this point of view, ammonium behaves exactly like the alkaline metals, which removes one of the objections with regard to the metallic nature of ammonium.—*Zeit. Physik. Ch.*, vol. xxxviii., p. 609.

Synthesis of the Aromatic Alcohols from Formic Aldehyde.—R. Stoermer and K. Bern.—Formic aldehyde unites with the aromatic phenols and their derivatives, being substituted in the radical in the form of an alcoholic residue:—

$$CH_2O + C_6H_5{<}^{CHO}_{OH} = (5)CH_2OH{-}C_6H_3{<}^{CHO(1)}_{OH(2)}.$$

In this way, 10 grms. of salicylic aldehyde shaken up with 15 grms. of commercial formic aldehyde and 50 grms. of concentrated hydrochloric acid, gave 25 grms. of *aldehydo-oxybenzylic alcohol*, in the form of silky needles, fusible at 105°, soluble in acetone, alcohol, and ether, slightly soluble in benzene and chloroform; it gives a violet colouration with $FeCl_3$ in aqueous solution, and has no reducing properties. When treated with hydrochloric acid and absolute alcohol, this body gives the *chloride*, $C_6H_3(OH)(CHO)(CH_2Cl)$, fusible at 88°. The *azine* of the alcohol fuses at 219°; it is a yellowish, crystalline powder, almost insoluble in the usual solvents, with the exception of alcohol; the *hydrazone* is a crystalline powder soluble in alcohol and fusible at 142°. The methyl ether, oxidised with $KMnO_4$ in alkaline solution, gives *methoxy-isophthalic acid*, from which we arrive at the constitution already given above. With the *o-homosalicylic aldehyde* we have obtained the alcohol $C_6H_2(CH_3)(CHO)(OH)(CH_2OH)$ 1 . 2 . 3 in the form of silky needles, soluble in the organic solvents. With salicylic acid very indefinite results were obtained. *o-Nitrophenol*, after boiling for six hours, gives the *oxynitrobenzylic alcohol* 1 . 2 . 4, in yellow needles, fusible at 97°, soluble in warm water and the usual solvents; at the same time a little *dinitrodioxydiphenylmethane* is formed. The *methylic ether* (1) fuses at 69°, it occurs in yellowish needles, soluble in boiling water; when oxidised by $KMnO_4$ it gives *m-nitroanisic acid*, fusible at 187°. The *chloride* (4) is in the form of yellow needles fusible at 72°, soluble in petroleum ether. The *o-chlorophenol* condenses with formic aldehyde in the cold, under the influence of hydrochloric acid gas, giving rise to the *chloride*, $C_6H_3Cl(OH)CH_2Cl$ 1 . 2, in crystals fusible at 93°, soluble in petroleum ether, transformed by boiling water into the corresponding *alcohol* in white needles, fusible at 123°, insoluble in petroleum ether and chloroform, but soluble in the other organic solvents.—*Berichte*, vol. xxxiv., p. 2455.

MEETINGS FOR THE WEEK.

TUESDAY, 13th.—Royal Institution, 5. "The Physiology of Digestion," by Prof. Allan Macfadyen, M.D.

WEDNESDAY, 14th.—Society of Arts, 8. "Industrial Trusts," by Prof. W. Smart, LL.D.

THURSDAY, 15th.—Royal Institution, 5. "Pre-Phœnician Writing in Crete, and its Bearings on the History of the Alphabet," by A. J. Evans, F.R.S.

FRIDAY, 16th.—Royal Institution, 9. "Low Temperature Investigations," by Prof. Dewar, F.R.S., &c.

SATURDAY, 17th.—Royal Institution, 3. "The Bi-centenary of Samuel Pepys—His Musical Contemporaries, Criticisms, and Compositions" (with Musical Illustrations), by Sir Frederick Bridge, M.V.O., Mus.Doc.

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THE CHEMICAL NEWS

Vol. LXXXVII., No. 2251.

RADIUM, POLONIUM, AND ACTINIUM.*

By WM. J. HAMMER.

Since the discovery a few years ago by M. Henri Becquerel of the remarkable uranium radiations which have since been known by his name, such an amount of attention has been given by physicists to the study of radiant matter, and to speculative theories as to the constitution of matter, that it will probably be some time before our views can settle down and adjust themselves to the new phenomena which have been presented and are daily being brought to our notice.

Becquerel demonstrated that compounds of uranium, and especially the metal itself, prepared in the electric furnace, possessed very great radio-activity. Thorium compounds, especially thorium oxide, are next in activity, though far weaker.

Mdme. Skiodowska Curie and M. Pierre Curie noted that other elements were inferior to these, and that the compounds were inferior to the metals themselves. Bohemian pitchblende and two other compounds of uranium suggested to them by their greater radio-activity to that of pure uranium, that some new substance existed more active than uranium, and after most exhausting and painstaking investigations, they discovered a metal identical with bismuth in its chemical characteristics, and far more radio-active, which they named "polonium" after Poland, Mdme. Curie's fatherland. A further search resulted in the discovery of another new metal very similar to barium in its chemical properties, which they called "radium," which was even far more radio-active. This was followed by the discovery by M. A. Debierne of a third element, which he has named "actinium," which has chemical characteristics similar to thorium. It has as yet not been fully demonstrated that these three are actually new elements, as none has as yet been secured in a pure state. (See note 1 of Appendix).

It is not my purpose to-night to go fully into the investigations which have been made in these remarkable substances, with which many of you are doubtless familiar; but in view of the interest which radium has excited in the scientific world, and as there are probably few in this audience to-night who have had an opportunity of seeing this remarkable, and up to the present time exceedingly rare, substance, I take pleasure in presenting a small quantity for your consideration, which I have secured through the courtesy of Prof. Dayton C. Miller, who imported the same from Paris. The tiny sealed glass tube which I hold in my hand contains about 1 grm. of radium, which cost in Paris about ten dollars.

I have prepared a few notes regarding certain properties of radium, which I will read, and which I trust will prove of interest,† after which, if the lights are put out, I will pass around the room, and you can observe not only the illumination produced by the radium itself, but also the radio-activity of the cotton which I will wrap around the tube.

An extensive dealer in chemicals informed me recently that the treatment of 5000 tons of uranium residues would probably not result in the production of a kilo. of radium. The present market price in this country is 4.50 dollars per grm., or approximatelly 2000 dollars a pound.

M. and Mdme. Curie and H. Giesel have succeeded in further purifying radium, and I understand that a preparation will shortly be on the market here at the cost of 35 dollars per grm. The chloride and bromide of radium are the most brightly luminous compounds, but all the salts are more or less radio-active.

The radium preparation which I am able to show you to-night differs from such substances as sulphate of lime and various compounds of barium, calcium, strontium, uranium, &c., which possess the property of glowing in the dark when exposed for some time to light, or are rendered active by electrical or heat vibrations, in that radium requires no such exposure to become incandescent, but will glow for months and even years, and also has the property of causing other substances near it to become radio-active, and to retain this activity in many cases for a long period. Radium has been called a constant source of "X" or Röntgen rays and cathode rays.

H. Becquerel estimates that the energy expended by radium is a few C. G. S. units per second, and a few ten-millionths of a volt, and that at this rate the loss of matter would be about 1 milligrm. in a thousand years. He also finds that the radio-activity of radium is 900 times that of metallic uranium, while that of polonium is only 400 times. (See note 2 of Appendix).

He also calls attention to the facts demonstrated by M. and Mdme. Curie and himself, that radium radiations carry negative charges like cathode rays, and like cathode rays also can discharge electrified bodies at a distance as well as render the air gap between the plates of a condenser conducting, and the current passing susceptible of measurement by an electrometer. Also that many bodies when exposed to radium influences acquire temporarily the power of rendering the air conducting and of discharging electrified bodies, all of which afford proofs of the contention that there is in reality a continuous emission of energy by transport of matter from radio-active bodies; and H Becquerel estimates the speed with which these particles are radiated at half to two-thirds the speed of light.

These investigations have also shown that radium radiations are of three kinds, a portion deviable by a magnetic field, a portion non-deviable and readily absorbed, and a third weaker portion of diffused, non-deviable rays attributable partly to secondary rays.

M. and Mdme. Curie state that the deviable rays have the greater penetrative effect, but constitute but a small portion, and that the non-deviable rays, which constitute the major portion, do not travel further in the air than 7 c.m. from the source. According to M. Becquerel there seems to be no difference in the deviable qualities of radium rays in the air or in a vacuum. M. and Mdme. Curie show that polonium only emits non-deviable rays, and that these only travel 4 c.m. from the source in air.

Giesel's polonium, on the contrary, emits both deviable and non-deviable rays; and J. Elster states that magnetic deviation of polonium rays is produced in a vacuum, and seems to exceed deviation of radium rays under same conditions.

S. Meyer and E. R. Von Schweidler, in studying the absorption of radium rays, call attention by plotted curves to the fact that the first few hundredths of a millimetre are most effective in the absorption, and that it may be concluded that with radium rays, as in the case of Röntgen, uranium, and thorium rays, the radiations consist of a large number of rays of different nature.

According to M. and Mdme. Curie, radium rays act in many ways like light. They reduce silver salts, peroxide of iron, and bichromate of potash in presence of organic substances; but they also colour glass, porcelain, and white paper, and they transform greenish yellow platino-cyanide of barium into a brown variety.

Giesel had prepared platino-cyanide of barium with a

* A Paper read at the 159th Meeting of the American Institute of Electrical Engineers, New York and Chicago, January 3, 1902.

† Prepared from data given to the writer by Prof Curie, also data from compilations of E. E. Fournier D'Alba in *London Electrician, Science Abstracts* and other sources, these being abstracts of *Proceedings of Roy. Soc., Phil. Soc., Phys. Zeitschrift, Ann. der Physik, Deutsche Phys Ges Verh.*, Chem. News, *Comptes Rendus Soc. Francaise Phys. Bull., Journ. de Physique*, &c.; see also. Prince Kropotkin on "Unsuspected Radiations," in *The Nineteenth Century*, December, 1900.

trace of radium. This spontaneously became brown, and it then polarised light like tourmaline. He also found that this coloured rock-salt just as cathode rays do, or the vapours of alkaline metals, and furthermore showed that radium salts, brought near the temples, or to the closed eyes, produced a sensation of light.

M. Becquerel, referring to the chemical action of radium rays, says that radium and uranium rays act upon silver gelatino-bromide, but produce no effect upon Daguerre plates, or upon photographic papers, and says that colourations of glass, porcelain, paper, and certain crystals, as well as the painful physiological effects, also belong to this class of phenomena. He also calls attention to the transformation of white into red phosphorus in twenty-four hours, the reduction of mercuric chloride in the presence of oxalic acid with the precipitation of calomel, and finally the destruction of the germinating power of seeds after long exposure.

Becquerel also shows that radium rays possess the same power as the electric spark, or the prolonged action of violet or ultra-violet rays, of restoring the phosphorescent properties under exposure to heat of a body deprived of them by over-heating.

O. Behrendsen found that by cooling radium in liquid air its radio-activity was reduced more than one-half. On heating again to a normal temperature, a slight increase of radio-activity was discovered, thus agreeing with the behaviour of phosphorescent bodies described by Lumière. (See note 3 of Appendix).

Curie and Debierne state that while all bodies become radio-active when placed in a closed vessel with solid salt of radio-active barium, this effect may be increased 40 times and made more regular by using the aqueous solution instead of the solid salt.

M. A. de Hemptemne, who discovered that gas which becomes luminous at a certain pressure under the influence of electrical vibrations becomes luminous at a higher pressure when exposed at the same time to "X" rays, also found that air which became luminous only at an exhaustion as low as 33 m.m., became luminous at a pressure of 44 m.m., brought into proximity with a radio-active substance, and at the same time the colour of the light changed from reddish violet to yellowish green.

Dr. C. Runge, the great German specialist, found that radium gave three distinct lines belonging to no other element. Demarçay had previously given these lines, together with some twelve others which he claimed to belong to radium, but thus far had not been proved to belong to radium. (See note 4 of Appendix).

Radium rays, like Röntgen or "X" rays, produce serious physiological effects. This was first demonstrated by Messrs. Walkoff and Giesel, the latter having kept on his hands for two hours a celluloid capsule containing radiferous barium bromide. The rays acting through the celluloid caused a light redness of the skin, and two or three weeks later inflammation set in, and the skin finally sloughed off.

M. Curie repeated Giesel's experiment upon himself, using radiferous barium chloride, acting through a thin sheath of gutta-percha, upon his hand. The activity of the substance was comparatively feeble, being about 5000 times that of metallic uranium. The rays left a red spot on the hand 6 c.m. square, which appeared like a burn, but gave no pain. In a few days the redness increased, and on the twentieth day crusts formed, ending with a sore which needed dressing. On the forty-second day the epidermis commenced to form on the edge, and fifty-two days after the action 1 square c.m. remained sore and of a greyish colour.

M. Becquerel, on carrying a small sealed tube containing a few decigrammes of very active radiferous barium chloride, the activity of which is 800,000 times that of uranium, underwent an experience of the same kind. The matter enclosed in the glass tube occupied a cylindrical volume of from 10 to 15 m.m. by 3 m.m. in diameter; the tube, wrapped in paper, was kept in a small paste-board box. On April 3 and 4, this box was placed several times in a corner of a vest pocket for a period, the total duration of which amounted to six hours. On April 13 it was perceived that the radiation through the tube, the box, and the clothes had produced a red spot on the skin, which became deeper as the time passed, marking in red the oblong form of the tube, and assuming an oval form 6 c.m. long by 4 c.m. wide. On April 24 the skin fell off; then the part most affected sank in, beginning to suppurate; oleo-calcareous dressings were applied to the sore for a month, the diseased tissues were removed, and on May 22, that is to say, forty-nine days after the action of the rays, the ulcer closed, leaving a scar which marked the placed of the tube.

"While care was being given to this burn," he says, "there appeared about May 15 a second oblong red spot opposite the other corner of the vest pocket in which the active matter had been placed. The exposure had been of short duration, an hour at most. Erythema now appeared, thirty four days at least after the exciting action; inflammation developed, presenting the appearance of a superficial burn; on May 26 the skin began to fall off; on receiving the same care as the first, this burn appeared to be more rapidly cured.

"In the interval of these observations, on April, 10, 11, and 12, the same tube of active matter, enclosed in a lead tube, whose walls were about 5 m.m. thick, was kept for forty hours in another vest pocket, but has so far been attended with no physiological effect."

"It may be added that Mdme. Curie, by carrying in a small sealed tube a few centigrammes of the same very active matter which had caused the effects described above, had similar burns, although the small tube was enclosed in a thin metallic box. In particular, an exposure of less than half-an-hour produced at the end of fifteen days a red spot, resulting in a blister similar to a superficial scald. Fifteen days were required for the cure. These facts prove that the duration of the effects varies with the intensity of the active rays, and with the duration of the exciting action."

"Our hands have been also affected. There has been a general tendency to desquamation, the extremities of the fingers which have held the tubes or capsules containing active products become hard and very painful. In the case of one of us, the inflammation of the extremities of the fingers lasted about fifteen days, and indeed, after the falling off of the skin, the painful sensations have not yet completely passed away at the end of two months."

As illustrating the action of radium rays upon bacteria, E. Aschkinass and W. Caspari speak of exposing cultures of *Micrococcus prodigiosus* to a radium preparation, and state that the rays killed the germs very effectively in about three hours.

Appendix.

Since presenting the above paper on radium, I have visited Paris and had the pleasure of spending some time at Professor Curie's laboratory at the Ecole de Physique et de Chimie Industrielles, and Professor Curie has shown me some very interesting experiments and apparatus. I asked him to criticise the matter which I had prepared, and he very kindly gave me in writing the following notes which are numbered 1, 2, 3, and 4, and refer to the paragraphs in my notes which are similarly numbered.

Notes by Professor Curie.

1. It is well known to-day that radium is a new element characterised by a special spectrum. Radium has an atomic weight equal to 225. (Refer to the report given in the *Comptes Rendus* of July, 1902).

2. Radium, actinium, and polonium possess an activity which is a million times that of uranium.

3. I found, on the contrary, that radium emits exactly the same quantity of Becquerel rays when it is in the liquid air, as it does at the normal temperature of the atmosphere. The luminosity of the chloride of radium is

stronger in the liquid air than in the atmosphere at a normal temperature.

4. The spectrum of radium has been fully studied by Demarçay and the rays that he points out certainly belong to him.

I asked Prof. Curie whether there existed at the present time, or whether there has ever been made, a kilo. of radium, and was informed that during the past three years only between 500 and 600 grms. of radium had been manufactured, and that this included all grades of purity, and he also stated that radium, as a metal, did not exist, practically all which had been produced thus far being chloride of radium associated with barium; but he showed me a tiny tube of chemically pure chloride of radium, which he said was the only sample of it in a pure state that existed in the whole world. It was about the size of a buck shot and contained less than three one-hundredths of a grm., and on my inquiring its value I was told that it had any value that one wished to give it; but that 20,000 dollars could not buy it. It was with this sample of pure chloride of radium that M. Demarçay made his tests with the spectroscope, demonstrating that radium was a new element, for it showed no lines other than those characteristic of radium.

With this sample the atomic weight of radium was also determined to be 225, being considerably higher than that of barium, which is 157.

I saw at the laboratory of the Societé Centrale de Produits Chimiques, where the radium is manufactured, a similar tube of radium of a lower grade, there being still a considerable trace of barium in it, which tube had a value of 5000 dollars. Prof. Curie told me that he would not care to trust himself in a room with a kilo. of pure radium, as it would doubtless destroy his eyesight and burn all of the skin off his body, and probably kill him. He showed me the scars on his arm, one of which looked as if he had had a very serious ulcer, due to a radium burn, which, I understand, had taken fifty-two days to heal, and the other showed that the skin had been blistered and slightly scarred; the latter was caused by an exposure of but five minutes to some radium of very high activity; the more serious scar was due to an exposure of one hour and a-half to some radium of much lower radio-activity, approximately 5000. All of the radium manufactured in France is made under the supervision of Prof. Curie, and is tested and the samples classified by him. He informed me that whereas the best German product shows an activity of only 300 times the activity of uranium, the best commercial product which is at present on the market in France has 7000 times the activity of uranium, and this at present costs 100 dollars a grm. in Paris. Through the courtesy of Prof. Curie I was enabled to secure from the manufacturing laboratory a number of tubes of radium of varying degrees of radio-activity, and sample tubes of polonium of both bismuth-polonium metal and nitrate of bismuth and polonium, each possessing a radio-activity 300 times that of uranium, and tubes of pitchblende, uranium, uranium residues from which the radium is extracted, &c., I have also secured through the courtesy of M. Boulay, of the Societé Centrale, an interesting set of photographs made by radium rays.

Merck Products.—This well-known firm have recently issued a pamphlet giving further information, and the opinions of various medical men, concerning some of their recent preparations, many of which have been already noticed in the Chemical News. Among these we observe iodipin, dionine, bromipin, tannoform, and tropacocaine; the latter has been used in three manners, for eye diseases, in dentistry, and as an anæsthetic. It is of interest to see what a number of cases have been carefully examined in which one or the other of these, as yet, little-known drugs have been used; we trust this careful watching will continue, and that more of these products will be found to be both beneficial and trustworthy in their action.

NEW COLOUR REACTIONS WITH BORIC ACID.

By CHARLES E. CASSAL and HENRY GERRANS.

The authors find that an intense magenta-red colour is produced on treating solutions containing boric acid with curcumin—or ordinary turmeric itself—and oxalic acid, and drying the mixture on the water-bath. The colour is different to that obtained by the application of the ordinary turmeric test for boric acid, and the reaction is far more delicate, extremely minute quantities of boric acid being easily detected. The colour is practically permanent for several hours—not less than ten or twelve—and fades very gradually on long keeping. The colouring matter is readily soluble in alcohol and ether without alteration, but is destroyed by the addition of water in excess. On treatment with alkali an intense blue colour is obtained, which is different to that obtained on treating the "rose-red," colouring matter formed in the ordinary turmeric test, with alkali. In applying the test for the detection of free or combined boric acid in milk and other food products it is convenient as a rule to operate on an ash. The ash is treated with a few drops of (1) dilute hydrochloric acid, (2) saturated solution of oxalic acid, and (3) alcoholic solution of curcumin or turmeric, and the mixture dried on the water-bath and taken up with a little alcohol. In cases where the amount of boric acid is very small the substance, the ash of which is to be operated upon, should be made alkaline with solution of barium hydroxide prior to evaporation and incineration. Caustic potash and caustic soda and salts of potassium and sodium in *large* amounts interfere with the formation of the colouring matter.

The authors have successfully applied the test for the purpose of estimating boric acid.—*The British Food Journal*, Oct., 1902.

A COLORIMETRIC PROCESS FOR THE ESTIMATION OF BORIC ACID.

By CHARLES E. CASSAL and HENRY GERRANS.

The methods at present in use for the estimation of boric acid in articles of food are in many respects very unsatisfactory, and, owing to the want of delicacy of the reactions and processes involved, the amount of substance to be operated upon must always be large. The distillation method is lengthy, difficult to control, and uncertain—although the modifications introduced by various investigators have considerably improved the original process. The glycerin method introduced by R. T. Thomson, although capable of yielding fairly good results when the amounts of boric acid present lie between certain limits, and when the necessary precautions are *strictly* observed, is not reliable when somewhat small or unusually large amounts of boric acid have to be dealt with in such articles as milk, cream, and butter. In this process, when applied to these articles, the removal of the phosphates present is essential. With great care this can be effected—unless the amount of boric acid is very high, in which case separation of the phosphates is not completely attained—but there is always the danger of incomplete removal, and, on the other hand, the authors have also found that there is great danger of considerable loss of boric acid through the liability of the latter to be carried down with the calcium phosphate. There are also other objections which it is unnecessary to refer to at length.

The authors have carried out a large number of experiments with the object of devising a colorimetric process for the estimation of boric acid based upon the turmeric reaction. The "rose-red" substance produced by the action of boric acid on curcumin has been named

"Rosocyanin" by Schlumberger, who has shown that it can be obtained in the form of characteristic dark red crystals which have a greenish tint by reflected light. In the limited time at their disposal the authors have not been able to ascertain whether the magenta-red substance obtained by them in their oxalic acid and curcumin process, described in the previous note, is identical with Schlumberger's Rosocyanin, and they must leave the settlement of this matter to other investigators—with the observation that the colour obtained in the oxalic acid process is distinctly different to that which is formed in carrying out the ordinary turmeric test. Under the conditions to be subsequently described the intensity of the colour produced in the oxalic acid process is proportional to the amount of boric acid present, and the reaction is very delicate. The authors have therefore been able to base a method for the estimation of boric acid and borates in articles of food upon this reaction. The following is a description of the process as applied to milk, and this will serve as a convenient illustration of the method:—From 15 to 20 grms. of the sample are weighed in a platinum dish, treated with a saturated solution of barium hydroxide until the mixture is strongly alkaline, and evaporated to dryness in a paraffin bath at a temperature of about 105° C. The residue is well charred, broken up, made just acid with hydrochloric acid, and extracted with successive small quantities of hot water. The extracts are filtered into a 100 c.c. flask. The filter paper and its contents are transferred to the platinum dish, barium hydroxide solution is added to alkalinity, and the dish carefully heated in a Bunsen flame until the carbon has practically disappeared. The ash is dissolved in a little 25 per cent hydrochloric acid, the solution and washings transferred to the flask, and the whole made up to the 100 c.c. mark with water (Solution A). From 10 to 15 grms. of purified sand (obtained by igniting "silver sand," boiling this with 25 per cent hydrochloric acid, and thoroughly washing and drying) are placed in a porcelain dish, and mixed with 10 c.c. of the solution of the milk-ash (A). The use of such a medium as sand is essential in order to secure intimate and complete contact between the reacting substances at the drying point—which is the point of reaction. The mixture is made alkaline with barium hydroxide solution, and evaporated in the paraffin bath, the mass being stirred from time to time to ensure thorough incorporation. When dry the mixture is made just acid with 25 per cent hydrochloric acid and 2 c.c. of a saturated solution of oxalic acid, and 2 c.c. of an alcoholic solution of curcumin (1 grm. per litre), are well mixed in. The dish is placed in the paraffin bath, and is covered with a funnel, the stem of which is connected with a set of "potash bulbs" containing barium hydroxide solution, the bulbs being placed in a beaker containing cold water. Air is then gently aspirated through the apparatus until the mass in the dish is dry. An additional 1 c.c. of the curcumin solution is then added, well mixed with the sand, and the mixture again dried.

The colouring matter formed is now removed from the sand by treatment with successive quantities of alcohol or methylated spirit, the solutions obtained being filtered into a flask. The liquid in the "potash bulbs" is transferred to the sand in the porcelain dish and dried, care being taken that the mixture is alkaline with barium hydroxide. The mixture is treated as before with hydrochloric acid and the oxalic acid and curcumin solutions, and the processes of evaporation and alcoholic extraction repeated, the further yield of coloured alcohol being added to the alcohol solution first obtained. As a general rule this second treatment is sufficient to ensure that the whole of the boric acid present in the 10 c.c. of ash solution operated on has entered into the reaction. A standard colour is prepared by operating on 10 c.c. of a solution of boric acid of known strength (1 c.c. equal to 0·1 miligrm. of B_2O_3) in precisely the same manner, the coloured alcoholic solutions obtained from the standard being made up to 200 c.c. In producing the colour from the milk-ash solution the amount of the liquid should preferably be kept below 100 c.c. to allow of convenient dilution.

The coloured solution obtained from the milk-ash is diluted with alcohol or methylated spirit until the colour is of the same degree of intensity as that formed from the standard; and the amount of boric acid is arrived at by obvious calculation.

The colours are compared in two tubes of the same internal sectional diameter (about 1 c.m.) placed vertically against a white porcelain plate.

On comparing the two solutions it will occasionally be found that a certain amount of orange tint is exhibited by one or the other, due to the presence of curcumin in slight excess. When this is observed the tints must be made the same by the cautious addition of solution of curcumin to the solution which does not show the orange tint.

The results of a number of experiments made with known amounts of boric acid and borates show that the process is reliable and accurate.

According to the experience of the authors, free boric acid, when in solution, is far more easily lost by evaporation than appears to have been generally supposed. The use of the funnel and "potash bulbs" and the other precautions above mentioned are necessary to prevent small losses of boric acid.—*The British Food Journal*, Oct., 1902.

THE ACTION OF CARBON DIOXIDE ON THE BORATES OF BARIUM.*

By LOUIS CLEVELAND JONES.

In 1888 Morse and Burton described "A Method for the Separation and Determination of Boric Acid" (*Am. Chem. Journ.*, March, 1888, vol. x., pp. 154—158). I published an article in 1898 entitled "The Action of Carbon Dioxide on Soluble Borates" (*Am. Journ Sci.*, June, 1898, vol. v., pp. 442—446) an account of certain results not in accord with those of Morse and Burton. More recently (*Am. Chem. Journ.*, August, 1900, vol. xxiv.) Morse and Horn record at some length "preliminary experiments" made in an effort to substantiate the original analytical results of Morse and Burton.

I have waited for some time for the promised resumption of these experiments, and lest further silence be misunderstood, will show that the action of carbon dioxide and boric acid, in the presence of the one base—barium hydrate—both in the dry state and in solution, is that which I pointed out in my original paper, and, further, that these later experiments of Morse and Horn, correctly interpreted, completely substantiate this position.

The question is concerning the action of carbon dioxide gas upon a mixture containing boric acid and an excess of barium hydrate, viz., what part of the total barium is converted into carbonate, and, upon evaporation and ignition, how much, if any, of this barium carbonate is re-converted into borate? Indirectly, and stated differently, it is:—Can boric acid, when once separated, be brought into definite and weighable condition by the method recommended by Morse and Burton? (*loc. cit.*). Despite the title of the contribution of Morse and Burton, Morse and Horn now regard the separation of the boric acid "as the most, and in fact the only, important feature of their contribution."

The following is the entire description of that part of the process relating to the determination of the boric acid as originally given by Morse and Burton:—"The quantity of the dilute barium hydroxide solution" (about 25 c.c,) "which is equivalent to 25 c.c. of the standard sulphuric acid" (N/10) "is run into the flask, and the apparatus attached to a filter-pump." This is done preparatory to

* Contribution from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. xiv., p. 49

receiving the alcoholic solution of boric acid—a little over 75 c.c. "*Finally, the excess of the barium hydroxide is precipitated by passing into it a current of carbon dioxide; the contents of the flask are transferred to a platinum dish, evaporated to dryness, and heated to a constant weight over a triple burner.*"*

In my original article I made three claims:—First, that the metaborate of barium may be decomposed by gaseous carbon dioxide; second, that the boric acid thus "liberated" may be lost by volatilisation; third, that the metaborate of barium and the carbonate may interact at high temperatures with the loss of carbon dioxide. These facts preclude the use of the method described by Morse and Burton for the determination of boric acid. The more recent experiments of Morse and Horn not only substantiate these facts, but disclose a fourth objection to the use of this method for its original purpose, viz., the difficult dehydration of the metaborate of barium, concerning a mixture of which with barium carbonate, Morse and Burton originally said that it "being neither markedly hygroscopic nor capable of absorbing carbon dioxide, can be brought to a constant weight more readily than one containing oxide of calcium or magnesium."

The Decomposition of Barium Metaborate.—That barium metaborate may be decomposed by carbon dioxide in aqueous solution, is proved by my original experiments; and now is corroborated by those of Morse and Horn. These authors, however, urge that, in alcoholic solutions —78 per cent—the boric acid would be in the form of metaborate of barium only, and this should be unattacked to the extent of its insolubility. To test this point directly, carbon dioxide was passed into equivalent parts of barium hydrate and boric acid in 78 per cent alcoholic solution. The precipitate gave abundant evidence of the presence of carbonate, showing decomposition of the metaborate. The extent of this decomposition was determined quantitatively by determining the carbon dioxide in another similar precipitate. Barium hydrate and an excess of boric acid in a mixture consisting of 73 per cent alcohol, were treated in the cold for three hours with carbon dioxide. The precipitate was filtered, washed, and analysed for carbon dioxide with the following result:—

$Ba(OH)_2$ taken, 0·7883 grm.; B_2O_3 taken, 0·3576 grm.; excess B_2O_3, 0·0357 grm.; CO_2 found, 0·2042 grm.; CO_2 in total barium carbonate, 0·2024 grm.

Evidently the metaborate of barium in alcohol was completely decomposed by carbon dioxide and the boric acid *liberated*.

Another experiment was made as above, except that equivalents were taken, and the treatment with carbon dioxide was discontinued after thirty minutes. After stopping the flow of carbon dioxide, the mixture was boiled for three minutes, to remove any excess of gas. The precipitate was filtered, washed with 150 c.c. of hot water, and analysed for carbon dioxide. The result was as follows:—

$Ba(OH)_2$ taken, 0·4379 grm.; B_2O_3 taken, 0·1788 grm.; alcohol, 76 per cent; CO_2 found, 0·1135 grm.; CO_2 in total barium carbonate, 0·1124 grm.

Upon evaporating to small volume the filtrate from this experiment, boric acid in abundance crystallised from the solution. Under these conditions, then, well within the limits of the recommendations of the Morse and Burton process, it is clear that barium metaborate is completely converted into carbonate with consequent *liberation* of boric acid, and that alcoholic solutions in no way prevent the action.

It might be argued that, in an evaporating mixture containing barium carbonate and boric acid in 78 per cent solution, the reaction would be reversed after the volatilisation of the alcohol and the solutions became more concentrated. Indeed, Morse and Horn used this explanation (p. 110). To test this hypothesis, equivalent parts of barium hydrate and boric acid in alcohol were treated with carbon dioxide for two hours, the mixture evaporated to dryness, and the carbon dioxide remaining in the dry residue determined. The following results were obtained:—

$Ba(OH)_2$ taken, 0·4554 grm.; B_2O_3 taken, 0·1860 grm.; alcohol, 82 per cent; CO_2 found, 0·1018 grm.; CO_2 in total barium carbonate, 0·1169. This shows that even with the very strong alcoholic solution, which was used by mistake, about 90 per cent of the metaborate was converted into carbonate and remained as carbonate after bringing to dryness.

To demonstrate, in another way, the presence of boric acid after the treatment recommended by Morse and Burton, I have used the methyl alcohol flame test. Equivalents of barium hydrate and boric acid (I have used the word equivalents repeatedly, meaning quantities to form exactly the most important salt under discussion, viz., metaborate) were evaporated to dryness, methyl alcohol added and burned without getting the slightest indication of free boric acid. Again, equivalents of barium hydrate and boric acid were treated in alcoholic solution with carbon dioxide, the ethyl alcohol and water removed by evaporation, and methyl alcohol applied and burned with unmistakable indications of free boric acid—burning with a solid green flame.

Since free boric acid does not decompose barium carbonate upon evaporation, the question arises as to what is the temperature required to bring about this decomposition. The following experiment throws some light upon this point: Finely divided anhydrous boric acid (0·1925 grm.) and barium carbonate (0·5177 grm.) were mixed in a platinum crucible moistened with water and allowed to stand sixty hours. The contents of the crucible were then dried on a steam bath and afterwards heated for thirty minutes in an air bath at 350° C. The carbon dioxide remaining in the mixture was determined and found to be 0·0844 grm. Total CO_2 in $BaCO_3$ taken, 0·1154 grm.; CO_2 liberated by B_2O_3, 0·310 grm.; CO_2 displaceable with formation of $Ba_2OB_2O_2$ by B_2O_3 taken, 0·1210 grm. Therefore, 74·38 per cent of the boric acid taken, if still unvolatilised, remains uncombined—at 350° C.

From the foregoing experiments, then, it is obvious that carbon dioxide decomposes the metaborate of barium in either aqueous or alcoholic solutions, and a portion, at least, of this boric acid liberated not only remains uncombined after evaporating to dryness, but even upon heating to a high temperature.

Loss of Boric Acid by Volatilisation.—It is scarcely conceivable that a mixture of boric acid and barium carbonate in water should not lose an appreciable amount of boric acid on evaporation. Morse and Horn have found a detectable loss of boric acid from treating aqueous mixtures of barium hydrate and boric acid with carbon dioxide and evaporating. The carbon dioxide was stopped shortly after the alkaline colouration with phenolphthalein was destroyed. The quantity found by them is given, and varies from 0·0001 grm. to 0·00016 grm.; in one instance exactly 0·00012 on 0·0633 grm. of total boric acid present—

$$\left\{\frac{0{\cdot}00636+0{\cdot}02538}{2}\times 13{\cdot}77\right\}\div 3{\cdot}448=0{\cdot}0633 \text{ grm.}$$

The decrease in weight should be even more noticeable in the presence of alcohol, though Morse and Horn did not detect more than 0·0040 grm. B_2O_3 $[(1/14200)\times 50=0{\cdot}0040]$, and this only when the concentration of alcohol arose above 92 per cent. Amounts below one part in 14,200 they were not able to discover.

The actual amount of boric acid volatilised on evaporating such mixtures to dryness is, of course, small, but certainly appreciable. Furthermore, under the analytical conditions described by Morse and Burton, the greater loss of boric acid doubtless occurs with the escape of water of combination between the temperature 100° C,

* The italics, as in other quotations to follow, are mine.—L. C. J.

and that at which the boric acid completely replaces its equivalent of carbon dioxide in barium carbonate. This temperature I have shown by experiment to be at least above 350° C. On the other hand, as was shown in my original paper, under extreme conditions, by the use of methyl alcohol and a continuous current of carbon dioxide, it is possible to volatilise all the boric acid from a mixture of barium hydrate and barium metaborate.

The Interaction at High Temperatures of the Carbonates and Borates of Barium.—I have shown that the treatment recommended by Morse and Burton may result in a mixture containing barium carbonate and barium metaborate, or barium carbonate, barium metaborate, and boric acid, or, indeed, barium carbonate and *free* boric acid. Of these compounds, both the barium metaborate and boric acid retain water considerably beyond 100° C.

Morse and Burton assumed that they had, after evaporation, a mixture containing only barium carbonate and barium metaborate. Morse and Horn explain it as follows: "It may be urged that even if Morse and Burton had the metaborate in insoluble condition, and it had been sensibly attacked during the treatment with carbon dioxide, nevertheless, in the subsequent attempt to heat the dried [illegible] due to constant weight, the metaborate must have attacked the carbonate. It has *since* then come to light that *some caution* must be exercised in this part of the manipulation. In the original description of the method, it was simply stated that the residue was heated to constant weight over a triple burner. The practice then, and on the few occasions when the process has since been used, was to hold the burner in the hand and rapidly play the flame over the platinum dish in order to secure as uniform a temperature of the contents as possible. The object in using a triple burner was not to obtain a *very high temperature*, which is not necessary, but, rather, to employ a flame large enough to keep the whole dish hot. No difficulty was experienced, when the heating was conducted in this manner, in *quickly* obtaining *constant and correct weights*. Nevertheless, it must be admitted, the authors of the method did not at that time suppose that the temperature at which the meta salt will attack the carbonate is so low as it has since been found to be. The temperatures employed by Jones were evidently *far* above those to which Morse and Burton heated their mixtures of metaborate and carbonate."

The use of a triple burner to secure gentle and uniform heating is unusual. Indeed, Morse and Horne used it in experiment XIV. for a quite different purpose, *i.e.*, to secure a temperature which decomposed the carbonate and borate mixture present. That the temperatures employed by me in my original experiments were *not* "*far* above those" used by Morse and Burton, can be answered best by the words of Morse and Horn: "*At a full red heat* the meta salt attacks the carbonate with expulsion of carbon dioxide" (page 130). "The temperature at which a mixture of the metaborate and the carbonate of barium is stable, and which is still sufficiently high to insure the dehydration of the former, *appears* to be *just* under a red heat" (page 130). Morse and Horn do not, however, produce any evidence to show that the meta salt is dehydrated below red heat. In fact, their experimental evidence points the other way: "The experiment of heating the material, after treatment with carbon dioxide, until the weight fell below that calculated for a mixture of metaborate and carbonate, and then of exposing it in the air until the weight became very nearly constant, and finally, of removing the slight excess of weight by placing the material over calcium chloride or sulphuric acid, was many times repeated, and always with a satisfactory degree of success except in two cases. In these it was *suspected* that, *while some portions of the material had been heated high enough to decompose the carbonate, other portions had not reached the temperature required for the complete dehydration of the metaborate*; for it was observed that the weights gained in the air on these occasions far exceeded the calculated deficits." Evidently, the temperatures at which decomposition of the carbonate and dehydration of the metaborate of barium takes place, cannot be *far* apart when both processes are going on in the same crucible.

I quote further (page 133): "In general, it was found difficult, by heating in our bath, to bring the too great initial weight of the material down to that calculated for a mixture of metaborate and carbonate, though in one case (No. XXX.) this was accomplished by heating in the bath for three hours over three burners. The temperature on this occasion, however, rose so high that the thermometer was removed." The thermometer used registered as high as 550° C.

The conditions described above can only be accounted for in two ways, viz: (1) The metaborate has been decomposed by carbonate dioxide, though this treatment was stopped five minutes after the disappearance of alkalinity with phenolphthalein—and the barium carbonate has not at this temperature been decomposed; or (2) the metaborate still contains water.

A combination of both these explanations, doubtless, more nearly expresses the truth. Morse and Horn, however (page 134), seem to prefer the latter explanation. "This," they say (*i.e.*, the behaviour of the ignited mixture in experiment XXX), "led us to *suspect* that the temperature at which complete dehydration occurs and that at which the metaborate begins to attack the carbonate cannot be very *far* apart."

The experiments made by Morse and Horn in an effort to show how these mixtures can be "quickly" brought to "constant and correct weights" are interesting, but not conclusive. They proposed (page 119) "to determine also the effect of exposing these mixtures, after heating, in an atmosphere containing carbon dioxide," with the object of finding "the temperature at which it was presumed a mixture of the metaborate and the carbonate of barium is stable, or rather the temperature at which it becomes stable." All these experiments, and those in which the mixtures were exposed to the air and dried in a desiccator, prove nothing; in fact, Morse and Horn only draw inferences from them (page 134): "From this it appears probable that the more basic borate which is formed at high temperatures, is decomposed at ordinary temperatures by the carbon dioxide of the air and re-converted into the borate and carbonate. A similar absorption of carbon dioxide takes place when material whose weight has been reduced below the normal amount is re-heated in the bath at temperatures under 500° C. From this it is *inferred* that normal weights could be *quickly* obtained by first heating to a high temperature and then at a lower one, but we have not yet tried the experiment."

Those final and satisfactory weights which are sometimes obtained may be due to the presence of an excess of carbon dioxide or water, or both, in an amount sufficient to replace any boric acid volatilised in evaporation and especially with the water of hydration. That Morse and Horn did have present in these experiments at the beginning of evaporation some free boric acid—or, if it is preferred, a more acid borate—and a corresponding increase in the amount of carbonate, is certain, because in all these experiments of which the results are recorded, carbon dioxide was passed for not less than fifteen minutes, or when phenolphthalein was used as an indicator, usually for five minutes after the disappearance of the alkaline reaction.

In my original paper I suggested the use of phenolphthalein to prevent too great an excess of carbon dioxide and corresponding decomposition of the metaborate. In a recent experiment I have tested the action of a metaborate in alcoholic solution upon this indicator, and find that exact equivalents of barium hydrate and boric acid in 78 per cent alcohol give a decided alkaline reaction, and that this alkaline colouration disappears only when about 36 per cent more boric acid is added. It is clear that phenolphthalein gives indication, not when the excess of barium hydrate is converted into carbonate, but at a point

considerably beyond. Morse and Horn, then, were working with barium carbonate and an acid borate, and in many cases, most certainly, with barium carbonate and free boric acid.

If by accident—and I see no other way of doing it—the action of carbon dioxide is stopped just when the excess of barium hydrate has been converted into carbonate, still nothing is gained; for the experiments of Morse and Horn—if they show anything—make it clear that even these salts cannot be weighed with safety.

These experiments leave nothing more to be done to prove the impossibility of bringing to definite and constant weights the mixtures resulting from the method described by Morse and Burton. Furthermore, in the promised forthcoming continuation of this study by Morse and Horn, I see no possibility of any other deduction.

In conclusion, then, I reiterate :—

First.—Carbon dioxide decomposes the metaborate of barium in either aqueous or alcoholic solutions.

Second.—The boric acid liberated may in part escape during evaporation to dryness and especially before reaching that temperature at which it has completely re-combined with the barium, replacing carbon dioxide.

Third.—A mixture, containing barium carbonate and hydrated boric acid, or barium carbonate with the hydrated metaborate and boric acid, or even barium carbonate and hydrated metaborate, cannot with safety be brought to definite composition for weighing.

NITRITES IN SUGAR-WORKS PRODUCTS.

By MM. ANDRLIK and STANER.

Up to the present time no quantitative determinations of nitrites in sugar-works products have been published; it appears, however, as if these bodies may be of some importance.

We have made use of Pellet's method, which consists of decomposing the nitrites in aqueous solution by acetic acid and the double chloride of iron and ammonium. Under these conditions the nitrates are not attacked, and the nitrogen evolved comes entirely from the nitrites. We have confined our estimations to the products which might be supposed to be the richest in nitrites and nitrates; that is, to molasses and syrups, and occasionally to the "boiling."

No.	Acidity in c.c. of normal potash.	Nitrous acid. M.grms.	Nitric acid. M.grms.
1. Bohemian molasses	Alkaline	7	36
2. ,, ,,	,,	4	32
3. ,, ,,	,,	5	28
4. ,, ,,	,,	4	21
5. ,, ,,	,,	5	38
6. ,, ,,	,,	9	56
7. ,, ,,	,,	10	29
8. Hungarian "boiling"	1·5	9	39
9. ,, ,,	4·0	20	28
10. ,, ,,	6·5	32	74
11. Italian syrup	10·7	41	59
12. Hungarian syrup	10·5	not estimated	490

The three latter samples frothed strongly, while the remainder showed no such phenomenon.

The amounts of nitrous or nitric acids in the Bohemian products varied from 0·004 to 0·01 per cent, while they increased considerably for the Hungarian and Italian products, as did also the acidity, and then the frothiness was produced.

When considering this richness in nitrous or nitric nitrogen and the tendency to froth, and the fact that oxides of nitrogen are sometimes given off by the frothy fermentation of syrups, we are led to the conclusion that the presence of large quantities of nitrites ought to facilitate or perhaps bring on the frothy fermentations.

Claasen identified two kinds of frothy fermentation—according as the fruth occurred simply on the surface, or throughout the mass of the syrup; and in this latter case we observe that oxygen is absorbed while carbonic acid is given off; he considers that we have to do with a phenomenon of a chemical order, decomposition by oxidation.

Von Lippmann has even observed the froth in the alkaline products, and he attributes it to a phenomenon of a chemical order, with the absorption of oxygen; this opinion is shared by Herzfeld and by us. All syrups and molasses, without exception, contain a large number of ferments, and we cannot well understand these developing in very viscous liquids containing 90 per cent of dry material.

Perhaps this development is the initial cause of the phenomenon by modifying the composition of the juices or the syrups; but it is very probable that the froths are due more especially to a chemical decomposition.

We have observed in the gases given off by frothy syrups both carbonic acid and binoxide of nitrogen, and this same mixture has been obtained by heating the syrup; acetic acid has also been found. A boiling was sampled while frothing, and it was dissolved in water containing a little acetic acid; on boiling, 100 grms. of the original "boiling" gave 170 c.c. of gas, consisting of 52·3 per cent CO_2 and 32 3 per cent of NO. The water over which the gas was collected was strongly acid.

Samples of syrups, "boiling," and residues examined, contained the following, per cent :—

	I.	II.	III.
Dry matter	93·46	87·72	87·42
Polarisation	71·20	54·40	48·00
Saccharose	71 06	Omitted	51 70
Invert sugar (m.grms. of Cu)	0·045	0·51	0·40
Ash	8·23	9·33	13·37
Actual purity	76·20	62 0	59 00
Total nitrogen	1·49	1·85	2·22
Nitric nitrogen	0 074	0 059	0·491
Nitrous acid	0·032	0·041	Omitted
Acidity in c.c. of normal KOH	6 0	10·7	10·0

These three products are all frothy, and are distinguished by a strong acidity and a rather high proportion of nitrous nitrogen. On the other hand, they show a certain amount of caramelisation, so that sub-acetate of lead will not decolourise them; finally, these syrups are rich in nitrogen.

We can get the froth in an entirely normal molasses by adding a nitrite and acidulating with lactic acid; a gaseous mixture is given off, analogous to that observed by heating a boiling with acetic acid, since in 100 volumes we find 54·3 CO_2 and 38 NO. The swelling up of the mass is only temporary, and the froth simply remains on the surface after the gas has been given off.

Thus it seems as if we ought to look upon the froth as being produced, not only by an evolution of carbonic acid gas, but also by the binoxide of nitrogen from the decomposition of the nitrites.

These abnormal froths must be attributed to the composition of the beetroots, these being rich in nitrogenous matter through having grown on a soil rich in nitrates and having undergone, after harvesting, a transformation of part of these in nitrates into nitrites. For the juices containing nitrites to give a froth they must also be able to lose their alkalinity, and become acid during the concentration of the boiling.

This is what happens to the juices rich in acids, and to those obtained from beetroots which have been overheated or damaged; these same juices contain invert sugar, and by the decomposition of this latter they produce organic acids which saturate the remaining alkalinity. Thus the alkalinity disappears in the boiling, and the destruction of the invert sugar continues; the boiling becomes acid, giving rise to a fresh inversion. On the

other hand, the nitrates can be reduced to the state of nitrites by bacteriological action, either in the damaged beetroots, in the diffusion juices, or in the syrups. Thus we get an acid boiling, the acidity decomposes the nitrites, and the froth is produced.—*Zuck. Ind. in Bohmen.*, 1902, p. 229.

THE ACTION OF CHROMIC ACID ON PEROXIDE OF HYDROGEN.

By A. BACH.

With the object of obtaining more precise information as to the mechanism of the action of oxidising agents on peroxide of hydrogen, I have endeavoured to ascertain more closely, from the quantitative point of view, the manner in which chromic acid behaves with this body. In this paper I propose describing briefly the results I have obtained.

Chromic acid behaves differently with peroxide of hydrogen according as the reaction takes place in the absence or presence of an acid. In the former case chromic acid is liable to decompose limited quantities of the peroxide—with the formation of a brownish-red intermediate product*—without itself being reduced.

In the latter case the reaction takes place in such a manner that after the formation of the long-known blue, unstable product, there is a definite simultaneous reduction of both the chromic acid and the peroxide of hydrogen, with the disengagement of oxygen and the formation of a salt of chromic oxide.

Action of Chromic Acid on Peroxide of Hydrogen in the Absence of an Acid.

When we cause pure chromic acid to act on pure peroxide of hydrogen free from acid, the mixture takes a brownish-red colouration, which gradually disappears, with the disengagement of oxygen, giving place to the original colour of the chromic acid.

Quantitative experiments were carried out in the following manner:—

By decomposing an accurately weighed quantity of chemically pure bichromate of potassium by the exactly necessary amount of decinormal sulphuric acid, I obtained a solution of chromic acid containing 19·2 grms. of disposable oxygen in 10 c.c. of the solution. By means of this chromic solution I determined the exact strength of a solution of hyposulphite of soda, which, in its turn, served for estimating the strength of a solution of iodine. On the other hand, I prepared a solution of chemically pure peroxide of hydrogen, containing 5 milligrms. of active oxygen per c.c. After having introduced into the decomposition vessel of the apparatus previously described, various but accurately measured quantities of the peroxide solution, 10 c.c. of the chromic solution were added by means of a burette, and the vessel was shaken until there was no more gas given off. The volume of the liberated oxygen was noted, and the liquid resulting from the reaction was transferred to a foot glass, with the help of 150 c.c. of water, and the remaining chromic acid estimated iodometrically.

In this manner the following results were obtained:—

Disposable oxygen in the chromic solution.	Active oxygen in the peroxidised solution.	Oxygen given off.	Disposable oxygen in the solution resulting from the reaction.
M.grms.	M.grms.	M.grms.	M.grms.
19·2	5·0	4·62	18·81
19·2	10·0	9·20	18·40
19·2	15·0	14·17	18·63
19·2	20·0	19·46	18·76

* The formation of this intermediate product has been already observed by M. Berthelot, *Comptes Rendus*, vol. cviii., p. 477.

It can be seen from these figures that, in the action of chromic acid on peroxide of hydrogen in the absence of acid, an amount of oxygen is given off corresponding exactly with the active oxygen in the peroxide used.

Action of Chromic Acid on Peroxide of Hydrogen in the Presence of Acids.

Baumann (*Zeitschr. f. Angew. Ch.*, 1891, p. 135) has suggested a gasometric method for the estimation of chromic acid, based on the observation that, in the action of chromic acid on peroxide of hydrogen in the presence of sulphuric acid, 4 atoms of oxygen are given off for each molecule of chromic acid reduced. According to Marchlewski (*Zeitschr. f. Ang. Ch.*, 1891, p. 392) this observation is not altogether correct, inasmuch as in this reaction there is always a little less oxygen given off than is to be expected by Baumann's method. My personal experiments have confirmed Marchlewski's assertion, and show that for each molecule of chromic acid reduced there are 3·5 atoms of oxygen liberated.

These experiments were carried out with the same solutions and under the same conditions as those above, with this difference, that 5 c.c. of normal sulphuric acid were poured into the decomposition vessel at the same time as the solution of peroxide of hydrogen. The results obtained are given in the following table:—

Disposable oxygen in the chromic solution.	Active oxygen in the solution of peroxide.	Oxygen given off.	Chromic oxygen engaged in the reaction.		Proportion $CrO_3 : H_2O_2$.
			Gasometrically.	Iodometrically.	
M.grms.	M.grms.	M.grms.	M.grms.	M.grms.	
19·2	5·0	8·56	3·56	3·70	1 : 2·10
19·2	10·0	16·66	6·66	6·84	1 : 2·25
19·2	15·0	25·98	10·98	10·98	1 : 2·09
19·2	20·0	34·34	14·34	14·34	1 : 2·08
19·2	25·0	43·34	18·34	18·34	1 : 2·04
19·2	30·0	44·88	19·20 m.grms. (excess of peroxide).		1 : 2·00

The chromic oxygen engaged in the reaction was determined, on the one hand, by the difference between the oxygen given off and the active oxygen contained in the peroxide, and, on the other hand, by the iodometric method, as has been explained above. As soon as the amount of peroxide of hydrogen used exceeded that corresponding to the proportion $CrO_3 : H_2O_2 = 1 : 2$, the presence of peroxide in excess was detected in the product of the reaction by means of permanganate of potash. In this latter case the peroxide oxygen entering into the reaction was determined by the difference between the oxygen given off and the chromic oxygen used.

We see by this table that, in the action of chromic acid on peroxide of hydrogen in the presence of sulphuric acid, there is a simultaneous reduction of the two substances with the liberation of oxygen.

For each molecule of chromic acid 2 molecules of peroxide of hydrogen come into the reaction. Thus, the reaction ought to be expressed by the following equation:—

$$4CrO_3 + 8H_2O_2 + 6H_2SO_4 = 2[Cr_2(SO_4)_3] + 7O_2 + 14H_2O.$$

It is easy to show the quantitative side of the reaction between chromic acid and peroxide of hydrogen by the following simple gasometric experiment:—

We decompose a known quantity of any solution of peroxide of hydrogen, by means of an acid solution of permanganate, and measure the amount of oxygen liberated. Now, if we treat the same quantities of the solution of peroxide with chromic acid in excess, once in the absence of acid and once in the presence of sulphuric acid, we obtain in the first case exactly one-half, and in the second case seven-eighths of the amount of oxygen given off by the peroxide under the action of the permanganate. According to the difference it is easy to calculate the proportion $CrO_3 : H_2O_2$.

For example:—

	C.c. of oxygen.
5 c.c. of a solution of peroxide of hydrogen liberated with permanganate	36·8
5 c.c. of the same solution gave, with CrO_3 in the presence of sulphuric acid	31·4
5 c.c. of the same solution gave, with CrO_3, in the absence of acid	18·2
Chromic oxygen entering into the reaction ..	13·2

Ratio $CrO_3 : H_2O_2 = (13·2 \times 2) : (18·2 \times 3) = 1 : 2·09$.

Theoretical Considerations.

The manner in which chromic acid behaves with peroxide of hydrogen furnishes some important points for consideration with regard to the hypotheses relating to the mechanism of the action of oxidising agents on peroxide of hydrogen. I will only speak here of the hypotheses of Traube and of Berthelot.

We know that, according to Traube, the hydrogen and oxygen would be only feebly combined in peroxide of hydrogen. Consequently, when oxidising agents are caused to react on this substance, its hydrogen is burnt to form water, and its oxygen is liberated integrally in the free state.

According to this hypothesis, in the action of chromic acid on peroxide of hydrogen, the former should be reduced to the state of chromic oxide, and the latter should give off the whole of its oxygen in the free state. Now, we have seen that in the absence of sulphuric acid, the chromic acid is not reduced at all, and that the peroxide only gives off half its oxygen; that is to say, only its *active* oxygen.

In the presence of sulphuric acid there is certainly a reduction of the chromic acid, but the amount of this acid reduced is less than that necessary for the oxidation of the hydrogen from the peroxide of hydrogen decomposed. According to Traube's hypothesis, the reaction between the chromic acid and the peroxide of hydrogen in the presence of sulphuric acid should take place according to the equation:—

$$2CrO_3 + 3H_2O_2 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3O_2 + 6H_2O.$$

But we have seen that in reality it corresponds with the equation:—

$$4CrO_3 + 8H_2O_2 + 6H_2SO_4 = 2[Cr_3(SO_4)_3] + 7O_2 + 14H_2O.$$

Thus, there is *less* chromic acid reduced and *more* oxygen liberated than there should be according to Traube's hypothesis. The facts which have just been stated seem, therefore, to completely dispose of this hypothesis.

But M. Berthelot's hypothesis also is not compatible with these facts. If we try to explain the reduction of the chromic acid in the presence of acids, by the intermediate formation of a trioxide of hydrogen, we are obliged to admit that of the 8 molecules of peroxide of hydrogen that enter into the reaction, 6 unite with the 6 atoms of disposable oxygen of the chromic acid, to form the hypothetical trioxide of hydrogen, while the 2 remaining molecules of peroxide are reduced in some other manner, which appears to me to be very unlikely.

The indisputable formation of a superoxygenated derivative of chromium during the action of chromic acid on peroxide of hydrogen enables us, in my opinion, to explain the decomposition of the peroxide by the metallic oxides more or less rich in oxygen, in a very simple manner. We can admit, in fact, that there is formed first of all, as an intermediate product, a superoxygenated derivative, not of hydrogen but of the metal employed.

In some cases (U, V, Ti, Mo, W, Nb, Ta) this intermediate product is relatively stable and can be isolated; in other cases, such as Cr, it is only slightly stable, but its characteristic colouration places its formation beyond all possible doubt; in other cases again (Ag, Hg, Pt, Pb, Mn), the formation of the intermediate product is not made manifest by any outward sign.

The formation of this kind of superoxygenated products seems to play the same part in the so-called catalytic decomposition of peroxide of hydrogen as in the decomposition according to a definite equation.

These processes can be explained in the following manner:—

In both cases the same intermediate product is formed by the addition of the peroxide of hydrogen to the oxygenated metallic compound used.

In the absence of acids, the superoxygenated intermediate compound decomposes in such a manner that it loses the oxygen taken from the peroxide of hydrogen and re-forms the original metallic oxide.

In the presence of acids, the intermediate product undergoes a more decided decomposition with the evolution of oxygen and the formation of a salt. If the oxide employed contains "disposable" oxygen, that is to say oxygen in excess of that required to form a salt with the maximum amount (MnO_2, PbO_2, MnO_4H, CrO_3), this oxygen is given off at the same time as that from the peroxide of hydrogen, which causes the illusion of the simultaneous reduction of the metallic oxidiser and the peroxide of hydrogen. As a matter of fact, there is nothing but the more or less spontaneous decomposition of the superoxygenated product, formed by the fixation of the peroxide of hydrogen on the metallic oxide brought into the reaction.

To sum up, there is absolutely no reason to admit the existence of oxidisable hydrogen in the molecule of peroxide of hydrogen, as required by Traube's hypothesis. Another conclusion that may be drawn from the above-mentioned experiments is, that there is no fundamental difference between the catalytic decomposition of peroxide of hydrogen and its decomposition according to a definite equation.—*Moniteur Scientifique*, Series 4, vol. xvii., p. 26.

NOTICES OF BOOKS.

The Chemistry of the Terpenes. By F. Heusler, Ph.D. Authorised Translation by Francis J. Pond, M.A., Ph.D. London: J. and A. Churchill. 1902.

The constant and rapid growth of our knowledge of the chemistry of the terpenes makes the task of writing a monograph on the subject one of peculiar difficulty, while at the same time the usefulness of such a monograph, in collecting and systematising our knowledge, is beyond dispute. Dr. Heusler's work is a most favourable specimen of a text book on one branch of organic chemistry. It was originally written for the *Handwörterbuch der Chemie*, and was subsequently published in book-form with corrections and additions. In it only well established and authenticated facts and theories are recognised, and the treatment is remarkable for its breadth of view and absence of partisanship Hence, an admirably well-balanced and comprehensive survey of the whole subject is presented. The discussion of the derivatives of Japan camphor has been much restricted owing to the enormous amount of work which has been done in this region, and the great amount of space which would be required for the adequate consideration of the subject. Copious references to original publications are given throughout the book. The translator has introduced into the text a large amount of new matter, embodying the results of investigations which have been made public since the appearance of the German edition. This book will undoubtedly be the standard book of reference on the subject of the terpenes for some time to come.

Organic Chemistry. By W. H. Perkin and F. Stanley Kipping. New Edition. London and Edinburgh: W. and R. Chambers. Ltd. 1902.

This new edition of a handy book has been completely evised by the authors, and important additions have been

made to the first edition, some chapters having been entirely re-written. The characteristic features of this book—the emphasis of general principles rather than matters of detail, and the systematic and convenient arrangement of the text—have made it of unique value to the student of organic chemistry, for whom it provides an introduction of moderate difficulty to the subject. As instances of really excellent chapters may be mentioned those on the synthesis of ketones and fatty acids by the aid of ethyl aceto-acetate and ethyl malonate, and on optical and stereo-isomerism. The book fully deserved its favourable reception on its first appearance, and can be confidently recommended for general use.

Papers on Etherification and on the Constitution of Salts. By Alexander W. Williamson, LL.D., F.R.S., Alembic Club Reprints. No. 16. Edinburgh: The Alembic Club, and W. F. Clay. 1902.

The sixteenth volume of the Alembic Club Reprints contains Williamson's classical papers describing his researches on etherification and the constitution of salts. In the case of two papers read before meetings of the British Association, the short abstracts, which appeared in the reports of the meetings, are reprinted, as well as the papers themselves, in which the theory of etherification is elaborated, and the foundation laid for the theory of types.

The importance to the student of chemistry of being able to obtain access to the original papers of the pioneers of modern chemistry amply justifies the publication of these valuable reprints. Williamson's peculiarly clear and graphic treatment of his subject and directness of method make this particular volume both interesting and instructive reading.

The Testing of Chemical Reagents for Purity. By Dr. C. Krauch. Authorised Translation of the Third Edition By J. A. Williamson, F.C.S., and L. W. Dupre. London: Maclaren and Sons.

This is a translation from the latest German edition of Dr. Krauch's useful work, and contains some additions and corrections suggested by the author. The book includes, arranged in alphabetical order under the headings of the various reagents most commonly employed, details as to their examination for impurities and adulterations, short descriptions of their quantitative determination, their chief uses, and other chemical and physical data; thus incidentally comprising much miscellaneous general information, which will render it almost indispensable in the laboratory. One excellent feature, due to the translators, is the substitution for the numerous references to German text-books on chemical analysis the corresponding English works, which greatly increases its usefulness to English readers. The list of atomic weights at the end of the book requires revision, the values according to the latest determinations being in many cases different from those given, and solubility and other tables might well have been added. This work, which is essentially one of reference, should find a place in every laboratory, and will certainly be found concise and complete as well as handy for use.

Elementare Vorlesungen über Telegraphie und Telephonie. 2 Lieferung. ("Elementary Lectures on Telegraphy and Telephony." Part II.). By Dr. Richard Heilbrun. Berlin: Georg Siemens. 1902.

This small book contains three lectures on induction, electrostatics, and the chemical effects of currents. In the first lecture the somewhat difficult task of explaining the subject of magneto-electric induction and its applications has on the whole been satisfactorily performed. The second lecture, on electrostatics, presents no particular novelty of treatment, but follows the usual lines and describes familiar experiments and phenomena. The last lecture explains very briefly and simply the theory of electrolysis. This book, which is copiously and well illustrated, appears to be very suitable for the use of those who have no previous knowledge of the subjects dealt with.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Edited by Franz Hofmeister. Band III. 4-6 Heft. Braunschweig: Friedrich Viewig und Sohn. 1902.

The two most important papers in the November number of this journal are the first, on the existence in the liver of a ferment which is capable of decomposing glycogen, and another on casein. In the latter paper considerable information is given as to the acid properties, molecular weight, and conductivity of the casein from cow's milk, and also the preparation is described of a modification to which the authors give the name iso-casein, obtained from ordinary casein by drying at a temperature of 94—100° for from twelve to eighteen hours; the properties and behaviour of this modification are described in detail. The first paper discusses at some length the proofs of the existence and the quantitative determination of the activity of the diastatic ferment of the liver, and should do something towards elucidating the question as to the nature and action of this ferment.

OBITUARY.

HENRY EDWARD SCHUNCK, Ph.D., D.Sc., F.R.S., &c.

We regret to announce the death of Dr. Henry Edward Schunck, which occurred on Tuesday morning last, January 13th, at The Oaklands, Kersel, near Manchester, in the eighty-third year of his age. By his death Science loses a well known chemist, whose work on colouring matters has extended over many years.

Dr. Schunck was born in Manchester in 1820, and after completing his school education he was sent to Germany to study chemistry, with the ultimate intention of taking over the direction of his father's large print and calico works in Manchester. At Berlin, under Rose and Magnus, he made first-rate progress, and, finally, took the degree of Ph.D., under Liebig, at Giessen. On returning to England, Dr. Schunck engaged for some years in practical work, but finding this repugnant to his taste and inclination he gave it up, and devoted himself to pure science, his attention being directed more especially to the chemistry of colouring matters. Dr. Schunck's first research, "On the Action of Nitric Acid on Aloes," was carried out in Germany, and resulted in the discovery of a new and remarkable nitro-acid with curious optical properties; this he called "chrysammic acid." By the action of reducing agents on chrysammic acid a substance is produced resembling indigo blue; this is known as hydrochrysamide, and crystallises in blue needles with a coppery lustre. This body has formed the subject of many subsequent investigations.

The next subject investigated by Dr. Schunck was the class of substances contained in various species of lichens, and he read an important paper on this subject before the Chemical Society in 1842. Another paper on this subject appeared in 1846, "On the Substances contained in the Roccella Tinctoria," which derives its interest from the fact of its being that species of lichen from which the finest kind of archil dye is prepared.

From 1846 to 1855, Dr. Schunck was at work on the colouring matters of madder, then one of the most important dye stuffs used in calico printing, but which has been replaced since by artificial alizarin. In 1854, amongst other papers, Dr. Schunck read one "On the Action of the Ferment of Madder on Sugar," and he dis-

covered the interesting fact, unique in the history of fermentation, viz., the production of succinic acid.

The important subject, the formation of indigo blue, next occupied Dr. Schunck's attention, and in 1855 he read a paper on this subject before the Literary and Philosophical Society of Manchester. On the discovery of the artificial formation of alizarin in 1867, Dr. Schunck undertook an investigation of the products formed at the same time, and discovered, partly in conjunction with Dr. Roemer, three new bodies isomeric with alizarin, viz., anthraflavic acid, iso-anthraflavic acid, and anthrarufin, which, strange to say, have no dyeing properties whatever; and in 1874 he read a paper on "Methyl-alizarin and Ethyl-alizarin."

One of Dr. Schunck's most interesting researches was commenced in 1879, and the first communication on the subject was read to the Chemical Society in September of that year, entitled "On the Purple of the Ancients." This colour, which in ancient times was extracted from various kinds of sea shell-fish, and applied to the dyeing of linen and woollen fabrics, has been made the subject of numerous treatises.

Besides being a Fellow of the Chemical Society, Dr. Schunck was elected a Fellow of the Royal Society in 1850; he has also held the positions of Secretary, Vice-President, and President of the Manchester Literary and Philosophical Society, and was President of the Chemical Section of the British Association at its meeting in Manchester in 1887.

Dr. Schunck's funeral is arranged to take place on Saturday, the 17th inst. at St. Paul's Church, Kersal, at 1 o'clock.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 10.

A New manner of Manipulating Liquid Gases in Sealed Tubes.—H. Moissan.—Already noticed.

Decomposition of Calcium-ammonium and Lithium-ammonium by Chloride of Ammonium.—H. Moissan.—Already noticed.

Electrolysis of Chloride of Ammonium in Solution in Liquefied Ammonia.—H. Moissan.—Already noticed.

Action of the Ammonium Metals on Sulphuretted Hydrogen.—H. Moissan.—Already noticed.

New Treatment of Niobite; Preparation and Properties of Cast Niobium.—H. Moissan.—Already noticed.

Preparation of Tantalum in the Electric Furnace, and on its Properties.—H. Moissan.—Already inserted in full.

Attempt to Decompose Monochlorosulphonacetic Acid (Monochlorosulphonethanoic Acid).—Ch. Porcher.—Cinchonine and strychnine are very convenient for the decomposition of racemic chloro sulphonacetic acid. Thus, with only 45·75 grms. of acid, requiring 154·20 grms. of cinchonine, the solution made up to 4225 c.c. brings about a very distinct separation; 100 grms. of a first salt are precipitated in very fine crystals, the other 100 grms. remain dissolved, and they are extracted partially from the aqueous solution by means of several concentrations. The two salts of cinchonine thus obtained are purified by one or two crystallisations; both are strongly dextrogyre. When re-dissolved separately in water and treated with a slight excess of ammonia, the cinchonine is precipitated; it is filtered, and the filtrate concentrated on the water-bath at a temperature not higher than 50°; this also drives off the excess of ammonia. From the first salt of cinchonine a levogyre ammoniacal salt is obtained, from the second a dextrogyre salt.

Some Phenolic Urethanes of Piperidine.—M. Bouchetal de la Roche.—If to 2 molecules of piperidine we add 1 molecule of carbonate of ortho-chlorophenyl the mixture becomes heated; the reaction is completed on a boiling water-bath; on cooling, the urethane crystallises out. It is washed with soda, and re-crystallised twice in alcohol at 93°. In this manner colourless octahedral crystals are obtained, fusible at 119°, boiling at 148—149° under 273 m.m. From 1 molecule of carbonate of para-chlorophenyl and 2 molecules of piperidine, a yellow oily mass is obtained, which does not crystallise on cooling, but becomes solid on contact with a solution of soda; a body is formed, fusible at 65°, boiling at 218—219° under 23 m.m. Eight grms. of piperidine, mixed with 27·7 grms. of carbonate of penta-chlorophenyl, gives a body which solidifies on cooling. On crystallising in benzene, small white crystals are obtained, fusible at 123°, boiling at 259° under 11 m.m. It is slightly soluble in alcohol. The author also describes the preparation and properties of the ortho-, meta-, and para-cresylic urethanes of piperidine, the eugenolic urethane of piperidine, and urethane of thymol.

The Hydrogenases of the Blood, and the Catalytic Properties of Fibrin.—E. Pozzi-Escot.—Freshly prepared fibrin decomposes peroxide of hydrogen, but it loses this property after a time, or even immediately if heated to above 70°; certain salts, such as those of the heavy metals, and the nitrates and nitrites in strong doses, act energetically as paralysing agents. This singular property of fibrin has been characterised, up till now, by the vague expression "catalytic action"; catalytic actions have had their day as mysterious phenomena, and in most cases these actions can be shown to be definite chemical actions; however, no satisfactory explanation has been given as far as fibrin is concerned. If, however, we consider the origin of this substance and the powers possessed by the diastases to fix themselves with great energy to certain inert bodies, we see that it is only natural to expect that fibrin owes its catalysing power to the presence of an ion of hydrogen connected with a hydrogenase. The author has proved that the hydrogenases do exist in the blood, where their property of reducing agent is certainly very important.

An Important cause of Error in the Detection of Diastases.—E. Pozzi-Escot.—Already noticed.

Passive Iron.—A. Finkelstein.—The author has measured, by Nernst's method, the polarisation capacity and the resistance of passive iron; he has determined the potential of passive iron in contact with different electrolytes, as well as the curves of decomposition of solutions of iron in contact with iron electrodes. In this manner he has observed that passive iron is covered with a badly conducting layer, and that it behaves like an electrode of oxygen of variable concentration. The electromotive force of an electrode of iron with regard to a solution containing a constant quantity of iron is a function of the proportion of ferric ions to the ferrous ions. The electromotive force is lowered by additions of cyanide of potassium. The curve of cathodic decomposition of the ferric salts shows that the iron is deposited with the properties of a noble metal. The curve of the anodic polarisation of iron enables us to observe very distinctly the commencement of passivity. The corresponding potential does not depend on the acidity, and it diminishes with the richness of the iron in solution. The hypothesis, according to which the passivity may be explained by a layer of oxide, ought to be abandoned; it may be, on the other hand, that passive iron consists of trivalent iron in the metallic state.—*Zeit. Physik. Ch.*, vol. xxxix., p. 91.

MEETINGS FOR THE WEEK.

TUESDAY, 20th.—Royal Institution, 5. "The Physiology of Digestion," by Prof. Allan Macfadyen, M.D.

—— Society of Arts, 8. "Principles which should Guide all Applied Art," by G. F. Bodley, R.A.

WEDNESDAY, 21st.—Chemical 5 30. "Researches on Silicon Compounds—Part VIII., Interactions of Silicophenylamide with Thiocarbamide," by J. Emerson Reynolds. "Phenocycloheptane," by F. S. Kipping and A. E. Hunter. "On the Relation between the Absorption Spectra and the Chemical Structure of Corydaline, Berberine, and other Alkaloids" and "The Absorption Spectra of Laudanine and Laudanoxine in Relation to their Chemical Constitution," by J. J. Dobbie and A. Lander. "The Influence of Molybdenum and Tungsten Trioxides on the Specific Rotations of *l*-Lactic Acid and Potassium *l*-Lactate," by G. G. Henderson and J. Prentice. "Estimation of Ethyl Alcohol in Essences and Medicinal Preparations," by T. E. Thorpe and J. Holmes. "Carbon Monoxide as a Product of Combustion of the Bunsen Burner," by T. E. Thorpe. "Derivatives of *β*-Resorcylic Acid and of Protocatechuic Acid," by W. H. Perkin, jun., and E. Schiess. "Synthesis of Imino-ethers—N-Ethyl-, Methyl-, and Benzyl-benzimino-ethers," by G. D. Lander. "A Synthesis of 1.3.5-Triphenyl-2.4-dimethyl-cyclopentane and of 1.3.5-Triphenyl-1.2-methyl-cyclopentane" and "The Condensation of Phenylethylketone (Propiophenone) with Benzalacetophenone, and of Acetophenone with Benzalpropiophenone," by R. D. Abell. "Formation of Carbazoles by the Interaction of Phenols, in the Orthoketonic Form, with Arylhydrazines," by F. R. Japp and W. Maitland. "Dimorphism of α-Methylanhydroracetonebenzil" and "The Oxidation Products of the Methyl Homologues of Anhydracetonebenzil," by F. R. Japp and A. C. Michie.

—— Microscopical, 8. Annual Address by the President.

—— Society of Arts, 8. "The Metric System," by A. Sonnenschein.

THURSDAY, 22nd.—Royal Institution, 5. "Pre-Phœnician Writing in Crete, and its Bearings on the History of the Alphabet," by A. J. Evans, F.R.S.

—— Society of Arts, 4 30. "Indian Domestic Life," by John David Rees, C.I.E.

FRIDAY, 23rd.—Royal Institution, 9. "Recent Volcanic Eruptions," by Tempest Anderson, M.D., B.Sc., F.G.S.

SATURDAY, 24th.—Royal Institution, 3. "The Bi-centenary of Samuel Pepys—His Musical Contemporaries, Criticisms and Compositions" (with Musical Illustrations), by Sir Frederick Bridge, M.V.O., Mus.Doc.

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THE CHEMICAL NEWS.

Vol. LXXXVII., No. 2252.

MODIFICATIONS OF HEMPEL'S GAS-APPARATUS.*

By THEODORE WILLIAM RICHARDS.

The object of this paper is the description of some simple devices which make possible the accurate analysis of gases with a minimum of special apparatus.

I. *Absorbing Pipette.*

The essential feature of Hempel's method is the use of simply constructed vessels distinct from the measuring

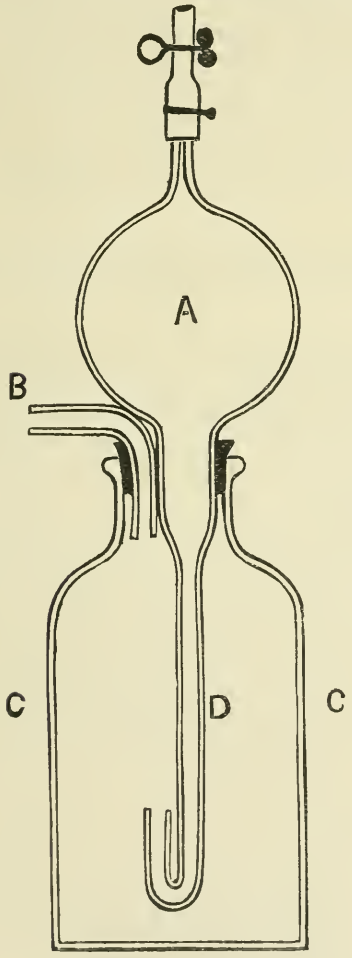

Fig. 1.

burette for the purpose of absorbing successively the various constituents of a gaseous mixture. Hempel used for this end a modification of Ettling's gas pipette, which answers the purpose admirably; but of course many other combinations of apparatus might be used. The simplest is perhaps a bulb or wide tube inserted over liquid contained in a bottle. In order to prevent the access of air into this bulb from below, it is well to make the lower part of the tube somewhat narrow, and to bend it upward. If desired, the capillary serving to admit the gas may be bent downwards and then upwards, as it is in the Hempel pipette; but with intelligent use of the pinch-cock this precaution is not necessary. A satisfactory form of the apparatus is illustrated in Fig. 1.

Fifty c.c. is quite enough gas for analysis, if a suitably narrow burette is used for measurement; hence the receiving bulb of the pipette (A) need not exceed 75 c.c. in capacity. The bottle (C) should be capable of holding 150 c.c. in this case.

The "compound pipette" of Hempel may be imitated by the addition at B of another bottle containing water and a levelling funnel, or the same object may be attained merely by connecting to the outlet B a flexible rubber bulb, such as a child's toy balloon.

For solids, the stem D of the pipette may be made of wider tubing, closed at the bottom with a perforated

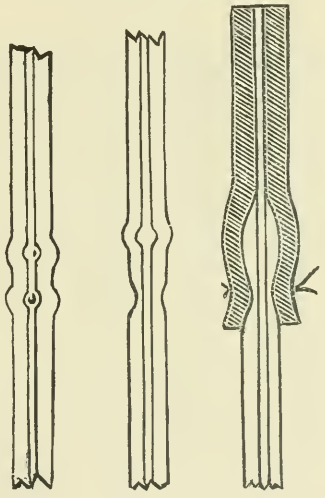

Fig. 2.

stopper. A small tube bent upwards may be inserted in this perforation, if especial precaution against incoming air is desired.

An explosion-pipette could be made of similar apparatus, with the addition of a stopcock just below the bulb A and the usual conducting wires.

The pipette for fuming acid might be made with a ground-glass joint instead of a stopper to connect bulb with bottle. In that case the bottle should be provided with a suitable side tube on the neck, bent upwards.

The method of using these pipettes will be understood without difficulty by any one familiar with the Hempel apparatus.

II. *Measuring Apparatus.*

The most serious cause of error in Hempel's ordinary apparatus is due to the possible change of temperature. This is considerably greater than the probable error in reading; for a single degree Celsius causes an error of 0·5 per cent of the total volume of gas measured under ordinary conditions, while the volume is easily read within 0·05 per cent. Hence, unless much greater care than usual is taken to preserve constant temperature, the reading of the volume is unnecessarily precise. But Hempel's ingenious arrangements for maintaining constant conditions in a 100 c.c. burette are so large as to be inconvenient for students' use in cramped quarters

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, vol. xxxvii., No. 10.

For these reasons I have often used somewhat smaller volumes, which may be surrounded with an envelope of water without producing thereby an unwieldly combination. An ordinary 50 c.c. burette, inverted and provided with a levelling bulb or funnel, answers very well as a measuring instrument. The burette may even be used in its usual position, if it is provided above with a smooth rubber stopper with a single hole for the capillary connecting tube. Of course the stopper is always pushed precisely into a definite position, indicated by a carefully made mark on the burette. There is little risk of displacing this stopper if it is firmly wired into place. In any case of course the ungraduated space at the upper extremity must be carefully calibrated. An especially made 50 c.c. instrument, graduated all the way to the capillary tube at the top, is more convenient, although no more accurate than the inverted burette. For convenience in cleaning, it is well not to have both ends of the burette drawn down to small diameter. The small size of the burette makes it easily possible to provide the water jacket which is so essential for accurate work, and both burette and pipette may be supported upon the ordinary iron ring-stand.

III. *Practical Operation.*

Of course the precautions usually necessary in gas analysis must be used in all the operations with this apparatus. For example, due time must be allowed for the running down of the liquid from the moistened walls. Again, care must be taken that the same amount of gas, at definite pressure (as small an amount as possible) is always left in the connecting capillary tubes. In order to make sure that no air-bubbles are caught, it is well to draw out the ends of the tubes in the manner illustrated in the diagram, which indicates two successive stages of the glass blowing, as well as the finished and connected nipple. The object of blowing the small bulbs is to render the bore of the portions drawn out as large as that of the rest of the tube.

While the apparatus thus constituted was devised primarily for use in an emergency, it has several advantages over the Hempel apparatus. It dispenses with the necessity of calibrating the whole length of a new burette, it is very inexpensive, and it occupies but little space. Each student may possess a complete set of apparatus, and every one knows the value from a pedagogic standpoint of such a possibility. A further advantage lies in the fact that the pipette is easy to fill and to clean; and a precipitate in the liquid is not apt to clog its working. The short straight capillary brings an obvious gain of speed in transferring. Moreover, because of this speed, and the fact that the pressure during transferrence is always from the outside inward, the danger of loss by leakage is considerably less than it is with Hempel's apparatus. It is well known that in a rubber tube an internal pressure may cause leakage, while an external pressure tends to stop small outlets by causing the rubber tube to be pressed more closely together.

On the other hand, the calculation is less obvious, because the volume taken is not just a 100 c.c.; and somewhat more care must be used to prevent the access of air into the pipette from below while shaking. A little practice enables one to shake thoroughly the liquid in the bulb without much agitation in the bottle if the movement is hinged about the point D; hence the danger is slight. Another slight difficulty is the possible leakage of the absorbent around the stopper of the pipette bottle—an unpleasant occurrence which has no effect upon the accuracy of the method.

In presenting for general use any new instrument one must record its practical working in the laboratory. Everybody knows that plausible inventions do not always stand the test of indiscriminate use. Accordingly a large class in gas analysis has been asked to use the new devices, with favourable outcome.

Analysis of known Mixtures of Air and Carbon Dioxide.

Volume CO_2 taken.	Volume air taken.	Volume air found.	Error.
c.c.	c.c.	c.c.	c.c.
16·95	32·02	32·01	−0·01
18·45	32·21	32·12	−0·09
12·20	42·20	42·20	±0·00
20·00	32·00	32·10	+0·10
14·90	37·60	37 60	±0 00
13 00	34·50	34·48	−0·02
16·50	36·50	36·55	+0·05

Excess of positive over negative errors, 0·03.

The pipette and burette were tested as follows:—A definite amount of air was run into the burette, and the volume measured with the usual care. Pure carbon dioxide was then run in from a generator, and the gain in volume was noted. This known mixture of air and carbon dioxide was run over into the new pipette, and after suitable shaking the residual air was returned to the burette and measured.

These figures, taken at random from among the results of the class, agree with one another as well as could be expected; and since the positive deviation balances the negative, there is no constant error. No trouble was experienced as to manipulation.

I am much indebted to Mr. Bisbee, the assistant, and to the gentlemen of the class in gas analysis, for their kindness in carrying out the practical trial of the apparatus.

THE GASES FROM SOME MINERAL WATERS.

By C. MOUREU.

I. Until quite recently, when making an examination of the gases given off by mineral springs, we have only accounted for oxygen, nitrogen, carbonic acid, sulphuretted hydrogen, hydrogen, and a few hydrocarbons.

Since the brilliant discovery of argon by Lord Rayleigh and Prof. Sir Wm. Ramsay in 1894, the attention of physicists and chemists has been drawn to the various gaseous sources met with in nature.

We may recall here the researches of M. Bouchard on the waters from Cauterets in 1895, our own practical experiments in the same year on the gas from Maizières (Côte-d'Or), and those of MM. Bouchard and Desgrez on the spring at Bagnoles-de-l'Orne in 1896.

The subject of this paper is the examination of five new sources of mineral gases. They are all situated in the Pyrenean regions. Four are in French territory; they are the springs at Peyré d'Ogeu (Lower Pyrenees), Nehe or Fontaine-Chaude, at Dax (Landes); Trou des Pauvres, at Dax (Landes); and Vieille, at Eaux-Bonnes (Lower Pyrenees); the fifth is the Saint-Augustin Spring, at the celebrated Panticosa station, situated at an altitude of 1650 metres, in Aragon, in Spanish territory.

In all these sources the gaseous mixtures are very rich in nitrogen, and make their escape spontaneously in more or less voluminous bubbles at the source of the spring.

The samples were collected and transported with all the necessary precautions to prevent their mixture with air, and we examined the various gases in the following manner in the laboratories of M. Moissan.*

II. A preliminary analysis is made first over mercury; the carbonic acid is absorbed by means of potash, and the oxygen with pyrogallate of potash. These two gases are always present in small proportions, and the residue has all the general characteristics of nitrogen.

* The gases from the two springs at Dax were collected and transported with the greatest care by M. Vielle, a well-known pharmacist in this town. We are equally indebted to MM. Cazaux, Espina y Capo, and E. G. Y. Echauri for their assistance at the springs at Eaux-Bonnes and Panticosa.

The argon and its allied gases can only be found in the residual nitrogen. The nitrogen is combined with calcium, and the new residue is submitted to spectrum analysis. In actual practice the raw natural gas was first left in prolonged contact with potassic hydrate and fused potash successively, being thus freed from carbonic acid and perfectly dried; it was then heated at a dull red heat, according to M. Maquenne's method, in the presence of an intimate mixture of 5 parts of anhydrous lime and 3 parts of perfectly dry magnesium, a mixture which fixes both the oxygen and the nitrogen at the same time. The spectroscopic examination was then made in Plucker tubes with aluminium electrodes, under a pressure of 2 to 3 m.m. of mercury.

III. The five samples of natural gas examined have all given non-absorbable residues, and each residue showed the characteristic argon lines in the spectroscope.

M. Deslandres was kind enough to complete this spectrum analysis, and he showed that in the gas from the Vielle d'Eau-Bonnes there was a certain proportion of helium, that rare gas which has been known for a long time to exist in the solar photosphere, and which was isolated by Sir Wm. Ramsay in 1895 from clèveite and some other minerals. From this same spring we may add that we have observed various lines in the spectrum which do not appear to belong to argon or to helium; these will be identified later on.

The following are the compositions, by volume, expressed in hundredths, of the different natural gaseous mixtures that we have examined. Each analysis is preceded by a few summary remarks on the corresponding water from the same spring:—

Spring at Peyré.—A lithia water containing 0·225 grm. of mineral matter per litre; temperature, 19·5°:—

Nitrogen	90·6
Oxygen	5·7
Carbonic acid	2·8
Argon	0·9

Spring at Nehe, or Fontaine-Chaude.—A water containing calcic sulphate and a little sodic chloride; 1·024 grms. of mineral matter per litre; temperature, 64°:—

Nitrogen	96·6
Oxygen	1·0
Carbonic acid	0·8
Argon	1·6

Spring at Trou des Pauvres.—A sulphurous water containing 0·576 grm. of mineral matter; temperature, 32°:—

Nitrogen	98·2
Argon and helium	1·8

(The analysis of this gas was made by M. Garrigou before the discovery of argon or helium, and he concluded naturally that it was pure nitrogen).

Spring at Saint-Augustin, Panticosa. — A siliceous water, rich in organic matter, containing 0·126 grm. of mineral matter per litre; temperature, 30°:—

Nitrogen	97·0
Oxygen	1·6
Carbonic acid	0 2
Argon	1·2

(This gas had already been analysed by MM. Saenz-Diez and Bonet; apart from the argon, which was not known at the time of their analysis, the results obtained by these two gentlemen are very close to our own).

We can see from the above that the gases from the five sources examined are very rich in nitrogen; all contain argon, while that from Eaux-Bonnes also contains helium.

It is interesting to compare these analyses with those already published of different natural gases. Such a comparison immediately draws attention to the spring at Maizières (Côte-d'Or) examined by us in 1896; the gas, which escapes from this spring in large bubbles, contains an enormous proportion of argon and helium (about 80 per cent), and is actually the richest source of helium known.

We may add that the interest attached to this class of research is far from being exhausted. Krypton, neon, and xenon, three other gases that Sir Wm. Ramsay has recently discovered in atmospheric air, may be expected to be met with; and for this reason there is a strong inducement to examine the various sources of natural gases very minutely.

The question also merits attention from another point of view. We know how complex is the problem of the action of mineral waters on the human economy; we are of the opinion that no point should be overlooked, and that in the present state of our scientific knowledge it would be at the least risky to refuse to any element a place in therapeutic action.—*Journ. de Pharm. et de Chim.*, Series 7, vol. xvii., No. 2.

THE INFLUENCE OF CARBONIC ACID ON DIASTASIC ACTION.

By O. MOHR.

The papers published by Baswitz in the *Berichte der Deutsch. Chem. Gesellsch*, in 1878 and 1879, are rarely referred to in spite of their importance. Baswitz has shown, as a matter of fact, that carbonic acid helps the action of amylase as a general rule; with certain starches we obtain no appreciable saccharification with small doses of diastase when carbonic acid is rigorously excluded; on the other hand, with other starches the saccharification reaches almost the same point, either with or without carbonic acid gas. Baswitz is of the opinion that in the latter case the starch contains substances capable of helping the amylase to the same extent as carbonic acid does.

I have endeavoured to decide whether the reaction of the starch is of any importance, by watching at the same time the effect of small additions of acids or of alkalis.

An emulsion was prepared of 2·5 grms. of air-dried starch and 200 c.c. of water, and the temperature kept at from 53°—55°. Five c.c. of cold extract of malt (5 grms. per litre of water) was added, and one portion left protected from carbonic acid, while the other portion was placed in an atmosphere of this gas, and both of them kept at 53—55° for two hours.

Both vessels were then plunged into boiling water, cooled, and made up to 250 c.c. The estimation of the maltose was made on 25 c.c., corresponding to 0·25 grm. of starch. All quantities of maltose less than 5 milligrms. in copper reduced, were termed traces.

The following experiment was made on six samples of starch; two had a neutral reaction, one slightly alkaline, one strongly alkaline, one acid, and one was soluble starch with a slightly alkaline reaction.

Starch. Reaction.	Maltose, per cent of dry matter of the starch. Without CO_2.	With CO_2.
I. Neutral	Traces	32·4
II. Slightly alkaline	,,	31·8
III. Strongly alkaline	,,	39 89
IV. Acid	About 10 per cent	25·56
V. Souble starch .. Slightly alkaline	,, 5 per cent	31·35
VI. Neutral	,, 8 per cent	29·51

The maximum amount of maltose was realised by a starch with a strongly alkaline reaction in the presence of carbonic acid.

From this we cannot conclude that the action of the carbonic acid has reached its maximum in giving 30 32 per cent of maltose, since sample III. has given nearly 40 per cent, and a portion of the carbonic acid gas has passed to the state of bicarbonate, thanks to the alkaline reaction of the starch.

The following series of experiments made with the neutral starch, No. VI., shows that the action of the carbonic acid is made still more favourable by the presence of asparagine. This sample being able by itself to effect the saccharification with very little asparagine, 0·01 for 250 c.c. of 1 per cent emulsion, the maximum is attained by the simultaneous action of the carbonic acid gas and some acid; with 0·05 of asparagine, the amount of maltose is almost independent of the carbonic acid, and finally with quantities of amides of 0·1 to 0·5 grm., the saccharification is slightly retarded by the carbonic acid; it is also less advanced than with smaller doses of asparagine. There is, therefore, an *optimal* dose for this substance.

The results obtained were as follows:—

Asparagine per 2·5 of starch.	Maltose per cent of dry starch.	
	Without CO_2.	With CO_2.
0·00	About 8·00	29·51
0·01	30·30	36·26
0·05	36·17	35·16
0·10	44·07	33·20
0·20	43·16	33·25
0·50	38·32	33·29

The following table gives the results obtained with increasing doses of lactic acid, with or without the simultaneous presence of carbonic acid:—

Lactic acid, per 2·5 of starch. M.grms.	Maltose, per cent of dry starch.	
	Without CO_2.	With CO_2.
1	34·78	17·87
2	23·57	12·69
20	Traces	Traces

The favourable action of lactic acid by itself is interfered with or reversed by carbonic acid, and this is confirmed by the fact that quantities of lactic acid of 2 m.grms. per 250 c.c. of solution, interfere with the production of maltose, and that 10 m.grms. stop the saccharification.

On the other hand, the liquefying action is in no way interfered with, which shows once again that liquefaction and saccharification are entirely independent.

Finally, we took the starches III., IV., and VI., and with them made 1 per cent emulsions, adding, at the same time, 1 m.grm. of lactic acid per 2·5 of starch; the experiments were then completed, with and without car bonic acid.

No.	Reaction.	Maltose, per cent of dry matter.	
		Without CO_2.	With CO_2.
III.	Alkaline	About 8 per cent	41·10
IV.	Acid	33·72	31·65
VI.	Neutral	34·78	17·87

We are enabled to draw the following conclusions from these experiments:—

1. The variations in the amounts of maltose formed by small quantities of diastase in the absence of carbonic acid do not appear to be due entirely to the reaction of the starch; still an acid action of the starch appears to be more favourable.

2. In the presence of carbonic acid, with the different starches experimented with, we obtain almost the same proportion of maltose, *i.e.*, 30 to 32·5 maltose, per cent of the dried starch.

3. The favourable action of asparagine is increased by carbonic acid if the acid is in very small quantity, and, on the other hand, it is interfered with if the dose is too great.

4. The favourable action of lactic acid is stopped by carbonic acid as soon as the optimal amount of lactic acid is exceeded. This optimal amount varies with the nature of the starch employed.

5. Carbonic acid has a favourable action only when using small quantities of amylase.—*Woch. fur Brauerei*, 1902, p. 94.

ON THE DETERMINATION OF LEAD IN ORES.*

By IRVING C. BULL.

The ordinary fire assay for lead in ores is frequently so erroneous in its results as to cause great dissatisfaction. With most ores the results are considerably too low (about 2 per cent) and with others notably too high, *i.e.*, in oxidised ores containing iron, copper, antimony, and bismuth the lead button may contain several per cent of such impurities, and so weigh more than warranted by analysis.

The object of this article, therefore, is to test and compare the best existing methods in order to select a method which may be recommended both because of its accuracy and rapidity. A number of schemes, gravimetric, volumetric, and electrolytic, have been proposed, but most of them have proven either too lengthy and troublesome or too inaccurate.

The first method which is to be examined, and which is to be taken as the basis of comparison with other methods, is the method of weighing the lead as lead sulphate. This method is to be tried upon six samples of lead ore obtained from different sections of this country and carrying various amounts of lead and impurities.

Each of these ores was first ground in an iron mortar, and then finished upon a bucking board until fine enough to pass through a hundred-mesh sieve; the last traces of ore not fine enough were ground in an agate mortar and passed through the sieve, then the whole was thoroughly mixed and quartered down to a small sample tube full of each ore, leaving about one quart of each ore in reserve. Again, the samples thus obtained were ground in an agate mortar to an impalpable powder, in order to get as complete solution of the ore as possible. It might be well to emphasise frequently that more errors are made by incomplete solution of the ore than is ordinarily supposed.

Weighed amounts of each of the ores were carefully spread over a watch-glass so as to expose as much surface as possible, and moisture in each determined by drying in an air-bath at 110° C. to constant weight. This work was performed so as to make, if necessary, any corrections in the lead percentages afterwards obtained. The moisture was as follows:—

1.	0·00	per cent
2.	0·36	,,
3.	0·25	,,
4.	0·42	,,
5.	0·32	,,
6.	0·14	,,

The sulphuric acid and other chemicals used were tested for lead, but none was found. Distilled water was used throughout.

The six ores were first assayed before commencing the work of comparison, so as to make this comparison as complete as possible. The assays were conducted as described in the "Notes on Assaying," by Ricketts and Miller, depending upon the character of the ore; *i.e.*, whether a sulphide, sulphate, or carbonate. Care was exercised in every case to obtain the best agreeing results. They were as follows:—

1. Galena	76	per cent
2. ,, ...	37	,,
3. Cerussite	9	,,
4. Sulphuret, galena, and sphalerite ..	24·7	,,
5. Galena and stibnite	28·7	,,
6. Cerussite	37·8	,,

* Contribution from the Havemeyer Laboratories, Columbia University. From the *School of Mines Quarterly*, xxiii., No. 4.

Part I.

A. *Gravimetric—Lead Sulphate.*

The following gravimetric methods were then carried out on each of the six ores, first weighing the lead as lead sulphate.

Method.—Dissolve three-tenths to one grm. of the finely-ground ore (depending upon the amount of lead in the ore) in 15 c.c. of concentrated nitric acid and a few drops of hydrochloric acid in a covered casserole or beaker, boiling until the ore is completely decomposed and the sulphur oxidised, adding more of each of the acids if decomposition seems to be incomplete. Cool slightly and add 10 c.c. of diluted sulphuric acid (sp. gr. 1·41) and evaporate to fumes of sulphuric anhydride. Near the end it is well to hold the casserole or beaker in the hand over the flame in order to prevent bumping and spattering; thick dense fumes of sulphuric anhydride are absolutely necessary to ensure complete conversion of the lead to sulphate.

Cool and add carefully 100 c.c. of distilled water, and boil for five minutes to dissolve any ferric salts that may have formed by evaporation. Cool and add 15 c.c. of 95 per cent ethyl alcohol, stir well, settle and decant through a small filter, leaving as much as possible of the residue of lead sulphate, calcium sulphate, barium sulphate, strontium sulphate, &c., in the casserole. Wash the residue thoroughly with a solution containing 1 per cent of sulphuric acid and 10 per cent. of alcohol, using about 400 c.c. in all; finally with alcohol alone, pouring the washings through the filter each time.

Dissolve the lead sulphate from the residue in the casserole in a strong hot solution of ammonium acetate, slightly acid with acetic acid; pour the solution through the filter into a clean beaker. The filter is best moistened with ammonia in order to form ammonium acetate with the free acetic acid in the ammonium acetate solution, in contact with the few particles of lead sulphate on the paper, and so bringing them in solution much easier. Repeat this until all the lead sulphate is dissolved, then wash the contents of the casserole on to the filter, first with dilute ammoninm acetate and then with hot water. The reaction which has resulted is as follows (Treadwell, *Qualitative Analysis*, p. 144) :—

$$2PbSO_4 + 2NH_4C_2H_3O_2 = Pb\begin{matrix}C_2H_3O_2\\C_2H_3O_2\end{matrix} + \begin{matrix}SO_2{-}O{-}NH_4\\O\\O\\SO_2{-}O{-}NH_4\end{matrix}>Pb\ .$$

Acidify the filtrate with sulphuric acid, adding alcohol as before, and filter upon a Gooch crucible. The Gooch crucible is fitted carefully with two layers of quantitative filter-paper in the bottom, then a very thin layer of asbestos, previously washed with dilute sulphuric acid, was laid on top of the filter-paper, making about three-sixteenths of an inch over all. This was sucked down by a strong suction as tight as possible, then dried in an oven at 110° C. to constant weight. The solution containing the lead sulphate was then filtered through, starting the suction very slowly and wetting the asbestos before starting, then washing the precipitate as previously described, and finally with absolute ethyl acohol, using considerable quantity. The crucible (and precipitate) is again dried at 110° C. in an air-bath, and weighed.

$$\frac{\text{Weight of lead sulphate} \times 0{\cdot}6829}{\text{Weight of ore taken.}} = \text{per cent lead.}$$

The method of filtering on a filter-paper, burning off the paper and igniting as described, generally was found to be very inaccurate as well as troublesome in manipulation; it was, therefore, filtered on a Gooch crucible, which simplified matters considerably.

The results obtained by this method upon the ores taken were as follows, which agreed more closely than those obtained using the old way of weighing the lead sulphate:—

1.	78·68	per cent
	78·62	,,
	78·65	,,
2.	37·20	,,
	37·26	,,
	37·22	,,
3.	10·76	,,
	10·74	,,
4.	18·43	,,
	18·40	,,
5.	27·25	,,
	27·21	,,
6.	38·50	,,
	38·54	,,
	38·51	,,

B. *Gravimetric—Lead Chromate.*

Proceed in this method exactly as described in the preceding method until the lead sulphate is dissolved in ammonium acetate. This solution is then brought to boiling and a fifth normal solution of potassium dichromate run in until all the lead is precipitated, and the solution above the precipitate, when the latter settles, possesses the dichromate colour. Then the solution is boiled vigorously for three minutes and filtered upon a weighed Gooch crucible prepared as described in the preceding method. The precipitate of lead chromate should be washed thoroughly with hot water until the washings possess no colour of dichromate. The same precautions should be observed here as in weighing the lead sulphate as described. The crucible and precipitate are then dried at 110° C. to constant weight. Too high heat must not be permitted in drying, as the filter in the bottom of the crucible will become charred and so give poor results. It is possible with the lead chromate to omit the layer of the filter-paper. The following are the results obtained by using the above method as described:—

1.	78·68	per cent
	78·71	,,
2.	37·28	,,
	37·30	,,
3.	10·77	,,
	10·74	,,
4.	18·45	,,
	18·40	,,
5.	27·23	,,
	27·20	,,
6.	38·47	,,
	38·50	,,
	38·48	,,

C. *Electrolytic—Lead Peroxide.*

Obtain the acetate solution of the lead in the ore in exactly the same way as described in the gravimetric lead sulphate method.

Dilute if necessary to a bulk of 200 c.c., add 20 c.c. of nitric acid (sp. gr. 1·35), warm to 60° to 65° C., and electrolyse with a current of $N.D._{100} = 1{\cdot}5—1{\cdot}7$ ampères; the electrode tension is without influence upon the condition of the peroxide, and may vary within wide limits. If the warming is continued during the operation, the precipitation of quantities up to 1 and 1½ grms. of lead peroxide is completed in about three hours, with larger quantities in about four to five hours. Complete precipitation is ensured by adding about 20 c.c. of water, and observing whether the freshly wetted surface of the electrode becomes darker. In case no blackening is observed at the end of ten to fifteen minutes, the current is stopped after removing the electrodes from the solution, and the precipitate is washed with water, finally with alcohol, and dried at 180° C., and weighed. The residue is anhydrous peroxide. The preceding method permits of the separation of lead from zinc, iron, nickel, cobalt, copper, gold, cadmium, mercury, antimony, and aluminium; in the presence of silver and bismuth, traces of

those metals in the form of peroxide pass over into the lead peroxide.

If the anode is roughened a greater amount of lead peroxide can be collected. Chlorine compounds must not be present in the solution for electrolysis. Manganese under the most favourable conditions is precipitated along with the lead, it being the only commonly occurring element that behaves similarly.

The following are the results obtained by proceeding with the method as above stated:—

1.	78·73	per cent
2.	37·35	,,
3.	10·80	,,
4.	18·58	,,
5.	27·32	,,
6.	38·60	,,

Part II.—Volumetric Methods.

D. *H. H. Alexander's Ammonium Molybdate Method.*

The decomposition of the ore and the method in general is followed exactly as in the gravimetric lead sulphate method as previously described, up to the point of dissolving the lead sulphate in ammonium acetate, instead of dissolving the lead sulphate from the other foreign sulphates upon the filter-paper; the filter-paper and the precipitate are put into the ammonium acetate solution, and digested for at least ten minutes in order to completely dissolve the lead sulphate; the solution should be acidified with acetic acid, diluted to 200 c.c. with hot water, boiled, and a standardised solution of ammonium molybdate run in from a graduated burette, until all the lead is precipitated, stirring the solution very thoroughly when near the end, and waiting a few moments before adding a drop of the solution to a drop of tannin solution as indicator. The tannin solution is prepared by dissolving one part of tannin in 300 parts of water. The first appearance of a yellow colour after adding a drop of lead solution to the tannin solution marks the end of the reaction. The excess of the ammonium molybdate necessary to affect the indicator (generally seven to eighth-tenths of 1 c.c.) must be determined and subtracted from the burette reading. This is done by taking an ammonium acetate solution of about the same strength and acidity, with no lead present; boil and titrate in the usual way, noting the quantity run in before affecting the indicator.

The ammonium molybdate solution contains 9 grms. of the salt per litre, and is standardised upon Kahlbaum's lead sulphate by dissolving in ammonium acetate, and titrating with the conditions as above stated.

To show the importance of prolonged boiling of the lead sulphate with a strong hot solution of ammonium acetate, acid with acetic, the following series of experiments were performed:—Took five different samples, 30 c.c. each, of a standardised lead acetate solution containing 0·010909 grm. of lead per c.c., and added to each portion 10 c.c. of a standardised solution of barium chloride, containing 0·005578 grm. of barium per c.c., then proceeding with each as described in the above method, titrating under the same conditions, but boiling for various lengths of time as indicated below.

	PbA sol.	Ba chloride sol.		Am. molybdate.
1.	30 c.c.	10 c.c.	boiled 2 mins.	30·20 c.c.
2.	,,	,,	,, 5 ,,	30·80 ,,
3.	,,	,,	,, 10 ,,	31·28 ,,
4.	,,	,,	,, 20 ,,	31·30 ,,
5.	,,	,,	,, 40 ,,	31·30 ,,

From the above, since 31·40 c.c. is the theoretical amount, it seems absolutely necessary to boil for at least ten minutes.

Interferences.

The important impurities that might occur in lead ore and so interfere with any of the methods here described are antimony, bismuth, barium, strontium, and calcium. Standard solutions of these elements were made up having the following strengths and compositions as indicated below.

	Grm.	
Barium hydroxide solution ..	0·005578	barium per c.c.
Calcium chloride ,, ..	0·00986	calcium ,,
Strontium ,, ,, ..	0·00984	strontium ,,
Bismuth nitrate ,, ..	0·00931	bismuth ,,
Antimony terchloride ,, ..	0·01005	antimony ,,

In standardising the above solutions the barium was weighed as barium sulphate, the calcium as calcium sulphate, the strontium as strontium sulphate, the solutions of the above three impurities (10 c.c. of each) being evaporated with sulphuric acid to dryness, and the sulphates weighed. The antimony was determined electrolytically, and the bismuth weighed as bismuth trioxide by precipitating as the basic carbonate of bismuth.

The following indicated amounts of the above five solutions were taken with a constant amount of lead acetate solution and carried out exactly as described in the above method with the following results; the theoretical amount of ammonium molybdate after allowing for indicator (eight-tenths of 1 c.c.) is 31·40 c.c.; in the following readings this allowance has been made:—

Antimony.

				Am. molybdate sol.
1.	30 c.c. PbA sol.	2·5 c.c.	Sb chloride sol.	31·40 c.c.
2.	30 ,, ,,	5 ,,	,, ,,	31·38 ,,
3.	30 ,, ,,	10 ,,	,, ,,	31·38 ,,
4.	30 ,, ,,	15 ,,	,, ,,	31·40 ,,
5.	30 ,, ,,	20 ,,	,, ,,	31·55 ,,

Bismuth.

1.	30 c.c. PbA sol.	2·5 c.c.	Bi nitrate sol.	31·40 c.c.
2.	30 ,, ,,	5 ,,	,, ,,	31·38 ,,
3.	30 ,, ,,	10 ,,	,, ,,	31·40 ,,
4.	30 ,, ,,	20 ,,	,, ,,	31·40 ,,
5.	30 ,, ,,	40 ,,	,, ,,	51·38 ,,

Barium.

1.	30 c.c. PbA sol.	0 c.c.	Ba chloride sol.	31·40 c.c.
2.	30 ,, ,,	5 ,,	,, ,,	30·90 ,,
3.	30 ,, ,,	10 ,,	,, ,,	29·20 ,,
4.	30 ,, ,,	20 ,,	,, ,,	27·30 ,,
5.	30 ,, ,,	40 ,,	,, ,,	35·80 ,,

Strontium.

1.	30 c.c. PbA sol.	2·5 c.c.	Sr chloride sol.	31·40 c.c.
2.	30 ,, ,,	5 ,,	,, ,,	31·40 ,,
3.	30 ,, ,,	10 ,,	,, ,,	31·10 ,,
4.	30 ,, ,,	15 ,,	,, ,,	30·35 ,,
5.	30 ,, ,,	20 ,,	,, ,,	29·70 ,,

Calcium.

1.	30 c.c. PbA sol.	2·5 c.c.	Ca chloride sol.	31·38 c.c.
2.	30 ,, ,,	5 ,,	,, ,,	31·38 ,,
3.	30 ,, ,,	10 ,,	,, ,,	31·35 ,,
4.	30 ,, ,,	15 ,,	,, ,,	31·38 ,,
5.	30 ,, ,,	20 ,,	,, ,,	31·35 ,,

By using the above method the following results were obtained upon the ores:—

1.	78·74	per cent
	78·82	,,
2.	37·41	,,
	37·44	,,
3.	10·80	,,
	10·83	,,
4.	18·47	,,
	18·51	,,
5.	27·44	,,
	27·35	,,
6.	38·66	,,
	38·58	,,

An attempt was made to improve upon the indicator used, but was without success in so far as reducing the

allowance for the end-point below eight-tenths of a c c. The following compounds were tried as indicators:—Ferrous sulphate and sulphuric acid, sugar, sodium thiosulphate and sulphuric acid, sulphurous acid, thioacetic acid, alkaloids with sulphuric acid (as morphine and narcotine), salicylic acid, potassium ferrocyanide, and ferricyanide. Of the above-mentioned compounds thioacetic acid proved to be the most encouraging as a distinct colour was concerned, but a greater allowance had to be made than with tannin.

E. *Koenig's Method.*

A complete description with details of the method was sent to us by Professor Koenig, of the Houghton School of Mines, where it has been used for a number of years although it has never appeared in any chemical journal. The following method is taken from Professor Koenig's description, which was followed exactly:—

Method.—Take three-tenths to 1 grm. of ore, depending upon the amount of lead contained therein, add 10 c.c. of concentrated nitric acid, and digest at a temperature between 60° and 100° C. until all brown gases have disappeared, and the ore is completely decomposed; this is accomplished more rapidly by frequent shaking or stirring. Pour liquid off, leaving the residue in the beaker, let go to dryness, but not hard dryness. Bring dry residue with 5 per cent sulphuric acid back into the flask, using about 50 c.c., boil for ten minutes, cool, let settle, filter, add again 50 c.c. of 5 per cent sulphuric acid to the precipitate, and decant as before; repeat this operation until about 450 c.c. of 5 per cent sulphuric acid have been used; thus we remove all soluble sulphates. Agitation of the liquid to promote contact with the solids is a vital requirement in order to remove these soluble sulphates. The filter should contain none of the solids. Add 50 c.c. of a 10 per cent solution of ammonium carbonate, let stand for twenty minutes, shaking very frequently, thus converting all the lead sulphate to lead carbonate. Filter through the same filter, and wash thoroughly with cold water until no trace of an alkaline reaction is exhibited in the wash-water.

Place filter-paper with the precipitate in a beaker, add 50 c.c. of a tenth normal nitric acid solution, stir, and digest well at about 50° C. for ten minutes. Add enough methyl orange indicator to produce a distinct red, but no more, and titrate the excess of nitric acid used to dissolve the lead carbonate with a tenth normal sodium hydroxide solution until a yellow colour is obtained.

Modifications.—Results were obtained with equal accuracy and greater rapidity by proceeding with the analysis exactly as in the gravimetric lead sulphate method up to the point where the lead sulphate is dissolved in ammonium acetate, and from that point on proceeding as described by Professor Koenig.

The following are the results as obtained on the ores, and although the results obtained do not vary much, if any, between the modification and the method as described by Professor Koenig, the time required for the manipulation of the modified method was less by about thirty minutes:—

	Prof. Koenig's.		*Modified.*	
1	78·58 per cent	1	78·60 per cent	
	78·62 ,,		78·64 ,,	
2	37·30 ,,	2	37 38 ,,	
	37·36 ,,		37·40 ,,	
3	10·65 ,,	3	10·58 ,,	
	10·60 ,,		10 62 ,,	
4	18·40 ,,	4	18·46 ,,	
	18 34 ,,		18·42 ,,	
5	27·15 ,,	5	27 24 ,,	
	27·20 ,,		27·26 ,,	
6	38·68 ,,	6	38·60 ,,	
	38·64 ,,		38·68 ,,	

The effect of the impurities upon the accuracy of the method as carried out in its modification is as follows:—The nitric acid having been calculated in each case from the back titration, the amounts of sodium hydroxide are not recorded.

Antimony.

		Nitric acid sol.
1.	30 c.c. PbA sol. 0 c.c. Sb chloride sol.	15·80 c.c.
2.	30 ,, ,, 5 ,, ,, ,,	15·82 ,,
3.	30 ,, ,, 10 ,, ,, ,,	15·80 ,,
4.	30 ,, ,, 20 ,, ,, ,,	15·80 ,,
5.	30 ,, ,, 40 ,, ,, ,,	15·80 ,,

Bismuth.

1.	30 c.c. PbA sol. 2·5 c.c. Bi nitrate sol.	15·80 c.c.
2.	30 ,, ,, 5 ,, ,, ,,	15·80 ,,
3.	30 ,, ,, 10 ,, ,, ,,	15·78 ,,
4.	30 ,, ,, 20 ,, ,, ,,	15·82 ,,
5.	30 ,, ,, 40 ,, ,, ,,	15·80 ,,

Barium.

1.	30 c.c. PbA sol. 2·5 c.c. Ba chloride sol.	16·32 c.c.
2.	30 ,, ,, 5 ,, ,, ,,	16·50 ,,
3.	30 ,, ,, 10 ,, ,, ,,	17·38 ,,
4.	30 ,, ,, 20 ,, ,, ,,	18·43 ,,
5.	30 ,, ,, 40 ,, ,, ,,	19·22 ,,

Calcium.

1.	30 c.c. PbA sol 2·5 c.c. Ca chloride sol.	15·85 c.c.
2.	30 ,, ,, 5 ,, ,, ,,	16·00 ,,
3.	30 ,, ,, 10 ,, ,, ,,	18·40 ,,
4.	30 ,, ,, 20 ,, ,, ,,	23·35 ,,
5.	30 ,, ,, 40 ,, ,, ,,	26·80 ,,

Strontium.

1.	30 c.c. PbA sol. 2·5 c.c. Sr chloride sol.	16·88 c.c.
2.	30 ,, ,, 5 ,, ,, ,,	17·50 ,,
3.	30 ,, ,, 10 ,, ,, ,,	21·50 ,,
4.	30 ,, ,, 20 ,, ,, ,,	25·50 ,,
5.	30 ,, ,, 40 ,, ,, ,,	28·88 ,,

F. *Oxalate or Permanganate Method.*

This method was first described by Hempel, then it was modified by Low as described in the *Journ. Am. Chem. Soc.*, October, 1893, also modified afterwards by Haswell, Crook, and Knight.

This method was carried out as follows, according to Low:—Decompose the ore, and wash precipitate of lead sulphate, calcium sulphate, &c., as described in the gravimetric lead sulphate method already given. Collect the precipitate of lead sulphate in a beaker free from filter-paper, and treat with 50 c.c. of a cold semi-saturated solution of ammonium chloride. Stir the mixture to dissolve as much as possible of the lead sulphate, and decant off the clear liquid; dissolve any lead sulphate in the residue with a few c.c. of a strong solution of sodium hydroxide, and heating to boiling. To this solution add sufficient dilute sulphuric acid to cause most of the lead to precipitate, avoiding an excess, and rinse back into the beaker containing the chloride solution. Place in the flask pieces of sheet aluminium, and boil for five minutes, whereupon all the lead is precipitated. Dilute with cold water, and decant, wash to remove chlorides. Finally, to the lead and aluminium in the flask add 5 c.c. of a mixture of one part strong nitric acid and two parts of the distilled water, and warm gently. The lead is all dissolved, wash and remove all the aluminium strips, add to the solution a few drops of phenolphthalein solution, and then a very slight excess of strong sodium hydroxide. Now add 10 c.c. of a cold saturated solution of oxalic acid. Cool if warm, filter, and wash thoroughly with cold water. In a beaker have heating about 75 c.c. of distilled water and a few c.c. of strong sulphuric acid; drop filter-paper and precipitate of lead oxalate into this solution, and titrate at once with permanganate. The factor for the iron times 1·888 gives the factor for lead.

Notes.—The method gave very poor results on the ores, as is shown by the following analysis of the ores; in fact the results were so inaccurate that the method was at

once condemned and the effect of impurities were not determined.

1.	77·54	per cent
	77·60	,,
2.	36·71	,,
	36·62	,,
3.	9·92	,,
	9·98	,,
4.	17·54	,,
	17·65	,,
5.	26·28	,,
6.	37·38	,,

The chief trouble seems to be in the fact that the lead falls from the aluminium foil, thus going slowly in solution and being lost; therefore larger sheets of aluminium should be used. Besides there seems to be a constant galvanic action going on between the solution and the aluminium which also takes lead into solution. The solubility of lead oxalate is objectionable; this can be somewhat overcome by the use of ethyl alcohol, concentrated solution, and a large excess of oxalic acid. The method is exceedingly long and troublesome, requiring about two and one-quarter hours time for its manipulation. The great care required in washing the oxalate precipitate, the inconvenience of precipitating and washing the spongy lead (a modification which in most ores seems unnecessary) and other details of manipulation seem to more than offset the advantage of an inside indicator.

Crook's modification was to obtain the acetate solution as in the gravimetric lead sulphate method as already described, and then precipitate the oxalate directly with an excess of oxalic acid, and the excess of oxalic acid titrated with standard potassium permanganate after making the solution acid with sulphuric acid.

Knight's modification was to obtain the lead sulphate as usual and dissolve it in boiling dilute hydrochloric acid and filtered if much silica or barium sulphate is present, the solution diluted to 100 c.c., and the lead precipitated by granular zinc. The metallic sponge of lead is then washed with cold water, and dissolved in nitric acid, the acid neutralised with sodium carbonate, the precipitate dissolved in strong acetic acid, alcohol added, and the lead precipitated with oxalic acid. It is then filtered and washed, and the precipitate dissolved in strong sulphuric acid, and the freed oxalic acid titrated with potassium permanganate.

(To be continued).

Substitution of Fluorine for Oxygen in Iodylised Compounds.—R. F. Weinland and W. Stille.—The authors, in conjunction with M. Lauenstein (*Berichte*, vol. xxx., p. 866), showed that an iodate, such as IO_3K, for example, treated with hydrofluoric acid gives IO_2Fl_2K. The iodylised compounds of M. Willgerodt (*Berichte*, vol. xxvi., p. 357), that is to say those resulting from the substitution of an organic radical for the OH in IO_3H, behave in the same manner. If, for example, we make a hot saturated solution of iodylobenzene $C_6H_5IO_2$ in hydrofluoric acid at 40 per cent, on cooling we obtain silky needles, or sometimes large, flattened prisms, which can be drained in a funnel on platinum gauze; these crystals are fairly stable in dry air, but decompose easily in moist air; they are decomposed by water into hydrofluoric acid and iodylobenzene, and if heated to 216° they decompose, often with violence. This body is fluoiodylobenzene, $C_6H_5IOFl_2$. In the same manner the ortho- and para-fluoiodylotoluenes, $C_6H_4(CH_3)IOFl_2$, can be prepared; the former is in small lamellary crystals, fusible at 120°, decomposing at 170—190°; the latter in beautiful crystals detonating at 198—206°.—*Berichte*, vol. xxxiv., p. 2631.

NOTICES OF BOOKS.

Quantitative Analysis. By Alexander Classen, Director of the Laboratory of Inorganic Chemistry and Electro-Chemistry in the Royal Technical School, Aachen. Authorised Translation from the Fifth German edition, with an Appendix on the Qualitative Analysis of Minerals, Ores, Slags, Metals, Alloys, &c., including the Rare Elements. By Norman F. Harriman, Assistant in Chemistry in the University of Michigan. With seventy-nine illustrations. Ann Arbor, Michigan: George Wahr, Publisher and Bookseller. 1902. Pp. viii., 540. 8vo. Ill.

The instructive writings of Professor Classen on methods in analytical chemistry have been before the public for nearly thirty years, his first publication ("Grundriss der Analytischen Chemie," Bonn, two vols.) being dated 1873, and passing to a second edition six years later. His "Handbuch der Analytischen Chemie," which appeared in two parts, one of qualitative and one of quantitative analysis, has also been through several editions in its original language as well as in translations into English, French, Polish, and Russian. Besides these, "Classen's Treatise on Electrolytic Methods in Analytical Chemistry," is well known in three languages.

The English version of the second part of his Handbuch, published in 1878, having been long out of print, Professor Harriman has been induced to prepare the present volume.

One of the features of Classen's book that makes it well adapted to the needs of those beginning the study of quantitative analysis, is the practical arrangement of the subjects treated; after a chapter on general operations, the author takes up first crystallisable salts, then alloys and minerals, and eventually advances to ores, slags, waters, &c., of increasing difficulty. The instructions in each example are very clear, being the result of long experience as a teacher and as an expert analyst. The section on pig-iron, steel, spiegeleisen, ferromanganese, &c., seems to be quite full, occupying forty pages; an equal number of pages is occupied with potable water and mineral waters, while the section on organic analysis is rather brief, as might be expected in a work of this description.

Volumetric analysis is treated separately (pp. 407—459), but the methods in this section are often referred to in the body of the work. Qualitative methods, with special reference to minerals, ores, slags, metals, and alloys, are described in a voluminous appendix. The volume closes with several useful tables and a full index.

The translator has done his share of the work with linguistic skill born of familiarity with German and an appreciation of the requirements of good English. He has strengthened the volume by introducing some processes that had been overlooked by the German author, notably the method for the proximate analysis of coal recommended by the Committee of the American Chemical Society, Handy's rapid volumetric method for phosphorus in pig-iron (titration of the phosphomolybdate precipitate), and some of the methods of that eminent expert on rock analysis, Dr. W. F. Hillebrand, of the U.S. Geological Survey, whose "Bulletin" is frequently cited.

While the volume contains no surprising novelties it will be found none the less usable on that account, and can be cordially commended to those needing a thorough work in instructing classes. Its clearly printed large pages make the book somewhat bulky, but it lies open well on a work-table; its illustrations are well chosen and sufficient for the purpose. H. C. B.

Physikalische Chemie der Zelle und der Gewebe. ("The Physical Chemistry of Cells and Tissues"). By Dr. Rudolf Höber. Leipzig: Wilhelm Englemann. 1902.

Owing to the rapid advances which are continually being made in the applications of physical chemistry in the

regions of physiology, it becomes more necessary every day for the physiologist to have a thorough and extensive knowledge of this branch of his subject. This book contains all that could be required for this purpose, and is in many respects an excellent work. A very clear and lucid exposition of the theory of ionisation will be found eminently worthy of careful reading, and the same may be said of the chapters on the theory of osmosis. If occasionally statements which should still be regarded as disputable are made in too definite language, as if their truth had been established beyond a doubt, the bold treatment of the whole subject atones for this characteristic defect.

Die Darstellung des Chroms und seiner Verbindungen mit Hilfe des Elektrischen Stromes ("The Preparation of Chromium and its Compounds by the Aid of the Electric Current"). By Dr. Max Le Blanc. Halle-a-S.: Wilhelm Knapp. 1902.

This is the third volume of the new series of monographs of applied electro-chemistry, and deals with the preparation of chromium and its compounds. In the preface the author alludes to the impossibility of making any report perfectly complete, however great the care bestowed upon it; it is obvious, however, from a perusal of this work, that every effort has been made to render it as comprehensive as possible, special attention having been devoted to the patent literature on the subject, which evidently has been carefully studied and most judiciously sifted to discover innovations of real importance, the main object being to obviate the necessity for frequent reference to original papers. The general plan and arrangement of the book are very similar to those of the preceding volumes of the series.

Die Chemische Industrie des Deutschen Reiches im Beginne des XX. Jahrhunderts. ("The Chemical Industries of Germany at the beginning of the Twentieth Century.") By Dr. Otto N. Witt. Berlin: Julius Sittenfeld. 1902.

The aim of this volume is twofold; firstly to summarise the state of the chemical industries of Germany at the beginning of the present century, with special reference to the part played by German chemical manufacturers in the Paris Exhibition of 1901, and secondly to commemorate the twenty-fifth anniversary of the founding of the "Verein zur Wahrung der Interessen der Chemischen Industrie Deutschlands," which sprang into existence in Frankfort in 1877, and celebrated its jubilee in September, 1902. The history of the growth in magnitude and importance of this society is closely bound up with the history of the chemical industries themselves, the interests of which it has done much to further. The book contains brief surveys of the present condition of the more important industries, together with short historical notices and copious statistics. Modern manufacturing processes are described as fully as space allows. The difficulties surrounding the judicious selection of the facts and details to be mentioned to the exclusion of others of apparently very nearly the same general interest and importance, are very great, but have as far as possible been surmounted in this volume, from which may be obtained a very clear idea of the present state of the German chemical industries.

Jahrbuch der Elektrochemie, VIII. Jahrgang. ("Annual of Electrochemistry, VIII. Year"). Edited by Dr. Heinrich Danneel. Halle, A.-S.: Wilhelm Knapp. 1902.

This is the eighth annual report on Electrochemistry, and is for the first time edited by Dr. Heinrich Danneel. No alteration has been made in the scheme or scope of the annual, though it has necessarily become somewhat more bulky, owing to the constantly increasing number of innovations and fresh processes and other developments of the subject, which cannot be allowed to pass by unnoticed. The report aims at being something more than a mere historical review, and sound criticism finds a considerable place in it. The editor has been aided in his task by distinguished collaborators, especially in the section devoted to Applied Electrochemistry. The part which deals with the purely scientific aspects of the subject has been written mainly by Dr. Danneell himself; it contains abstracts of papers of importance which have appeared during the year, together with critical notices of the most recently published books on Electrochemistry. Improvements and innovations in apparatus and instruments are also described. The section on the applied science contains copious lists of patents and is fully illustrated by diagrams; it also contains a complete list of recent books and articles bearing on the subject. Though not unnaturally the work of German chemists receives the greatest amount of attention, somewhat to the exclusion of those of other nationalities, the annual gives on the whole a comprehensive and satisfactory view of modern work in the region of Electrochemistry.

Jena Glass and its Scientific and Industrial Applications. By Dr. H. Hovestadt. Translated and edited by J. D. Everett, M.A., F.R.S., and Alice Everett, M.A. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1902. Pp. 419.

The Jena glass works owe their existence to the increasing demand for excellence in refracting instruments. Abbe pointed out in 1876 that since Daguet's glass-works were closed there were only two establishments left which supplied public demands, as the third one (the only one in Germany), founded by Utzschneider and Fraunhofer, was still in the exclusive service of one optical firm. As a result of these remarks Schott communicated with Abbe, and in 1881 they commenced a joint investigation of the difficult problem of how to improve optical glass.

The first meltings were very small—not more than 2 to 30 grms.—and were directed solely to the purpose of studying all chemical elements that could enter in any form into the composition of glasses, as regards their influence on refractive power and dispersion; thus a series of facts was ascertained which gave hopes of obtaining new kinds of glass, better for some purposes than ordinary crowns and flints. Some of the problems it was desired to solve were to obtain glasses of the same mean refractive index and very various dispersions, and glasses of the same mean dispersion and very varying refractive indices. The practical realisation of this must be expected to take place gradually, but very tangible results were already obtained in 1883.

When Abbe and Schott began their experiments there were only five glass-forming oxides whose optical effects were well known, but they gradually increased this number until twenty-eight new elements were introduced in quantities of at least 10 per cent. It was soon seen that by the introduction of new elements variation of the hitherto fixed relation between refraction and dispersion could be attained, and fluorine was found to be a most advantageous element to use, since, besides lengthening the blue end of the spectrum, it lessens the dispersion throughout the middle portion. As the Jena glass works have gradually developed, other branches of manufacture have been taken up, and glasses characterised by special powers of withstanding heat and chemical action have been produced; but in this regard we are sorry to notice a great falling off in the quality of glass during the last two or three years.

The Jena glass beakers we have had lately are in no way better than ordinary Bohemian glass, numbers of them crack simply through having water boiled in them; and though we were so well satisfied with them five or six years ago, we have been obliged lately to discontinue their use owing to the large number of breakages, and have returned to the use of ordinary Bohemian glass.

The bulk of this volume is of a decidedly mathematical character, and deals with optical systems, the mechanical, thermal, and optical properties of glass; after-working and thermometry; the chemical behaviour of glass surfaces; electric and magneto-optic properties of glass, &c.

The appendix contains a revised list of Jena optical glasses, and there are a number of additional notes on coloured glasses, Durax glass for gauge-tubes, influence of temperature on thermal conductivity, and the optical effects of stress, &c.

There is a short list of errata which must not be overlooked, and a good table of contents and an index.

Gas Analysts' Manual. By JACQUES ABADY, M.Inst.M.E. Incorporating F. W. Hartley's "Gas Analysts' Manual," and "Gas Measurement." London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1902. Pp. 561.

THOUGH the two above-mentioned books are incorporated in this volume, it will be found that the larger proportion of matter is new work, the bulk of Mr. Hartley's books being found in Chapters I., XI., and XII., which deal with "Photometry," "Meter Testing Apparatus," and "Meter and Governor Testing."

This volume is divided into twelve chapters, and an appendix containing a number of tables useful for working out results. As already mentioned, Chapter I. is on photometry, and describes with great detail the methods in vogue for making photometric tests, while emphasis is laid on the necessity for the periodical re-verification of standardised instruments. With regard to standards of light, the standard laid down by Act of Parliament for the United Kingdom, except London, is the well-known standard sperm candle, burning 120 grains per hour. Personally, we prefer any other standard light to this one; the "standard candle" is one of the most variable sources of light. The standard of light adopted in London is Harcourt's 10-candle pentane lamp, by which excellent results can be secured.

Of late years circumstances have arisen in connection with the manufacture and distribution of gas, differing in many respects from those of a few years ago.

Formerly, the principal use to which gas was put was to produce a luminous flame, but now heating power is becoming an important factor, not only for cooking purposes, but also for furnishing light by heating incandescent mantles; hence more attention is being paid to the calorific value of gas, and the most important question for the consideration of gas makers is how to produce a gas of adequate calorific power which will at the same time satisfy the statutory requirements as to lighting power. This subject is dealt with in Chapter IV. on calorimetry and specific gravity, and includes a note upon "Mond" gas.

It is claimed for "Mond" gas that it is a perfect power-gas, and when combined with the use of gas-engines, forms the cheapest, most scientific, and the most economical method of dealing with fuel.

The process differs from other methods of gas making in that all the carbon is converted into gas, and a large proportion of the cost of the fuel (up to 75 per cent) is recovered as sulphate of ammonia.

Chapter V. is on "The Referee's Test for Sulphur and Ammonia in Gas," and includes a full description of the apparatus used and the details of carrying out the tests. Chapter VI. is on "Coal Testing," and Chapters VII. and VIII. describe the various tests for enrichment, purification materials, and purity tests for the gas in various stages of manufacture.

The by-products from gas making have always been a most important item; these are dealt with in Chapter IX., while in Chapter X., which is one of the most useful in the book from the practical point of view, we find all the operations of technical gas analysis as are ordinarily in use in a gas-works. The complete analysis of such a complex mixture as illuminating gas is a most intricate operation, and does not come within the scope of routine gas examination; the methods in general use in gas-works are those necessitating the use of Elliott's or Hempel's apparatus, while the analysis of furnace gases is made either by Orsat Muencke's or by Bunte's apparatus.

The book is of undoubted value, and unites a large amount of hitherto scattered information in one volume. The index especially is to be recommended, and fills 35 pages.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 26, December 29, 1902.

Presence of Argon in Gases from the Bordeu Spring at Luchon, and presence of Free Sulphur in the same Sulphurous Waters.—Henri Moissan.—The author makes a quantitative analysis of the gases issuing from the Bordeu Spring at Luchon, and finds that they contain 2·56 per cent of argon in which there is no helium. Further experiments prove that the water of the grotto contains sulphur in solution.

A New Preparation of Silicon Hydride, Si_2H_6.—Henri Moissan.—When lithium silicide is gently heated in a current of dry hydrochloric acid gas, a certain amount of hydrogen is produced as well as chlorides of lithium and silicon. If, on the contrary, a concentrated solution of hydrochloric acid, $(HCl+2H_2O)$, is allowed to act slowly on the lithium silicide, siliciuretted hydrogen, Si_2H_6, is formed in abundance, and this can be condensed by allowing it to pass into liquid air at $-200°$.

Emanations from Phosphorus.—Eugène Bloch.—The conducting power of dry air when passed over phosphorus is due to ions of very weak mobility, which serve as nuclei of condensation for water vapour, even when the air is not saturated. The author puts aside for the moment the question of the chemical mechanism by which these ions are produced, and if their formation is allied to that of a definite compound, such as ozone or an oxide of phosphorus, or if it is due to a simple modification of the oxygen. This question is evidently connected with the precise chemical examination of the oxidation of phosphorus, on which subject a great deal of further research is necessary.

Spectrum of Flame.—C. de Watteville.—Flame spectra may be divided into two classes, those of pure calorific origin and those of electric as well as calorific origin. The study of the former has lately been neglected. The author examines the spectra of the two principal regions of a flame, the interior cone and the flame proper which surrounds this. His researches are made on flames formed by the combustion of a mixture of inflammable gases, and also of air charged with powders of metallic salts.

Proportion of Hydrogen in Atmospheric Air.—Anatole Leduc.—This paper is an answer to M. Gautier's discussion on the relative proportion of hydrogen in atmospheric air. The author re-investigates the matter, and finds no reason to change his former opinion.

Thermic Examination of Metaphosphoric Acid.—H. Giran.—The author measures (1) the quantity of heat evolved during the transformation of metaphosphoric acid into orthophosphoric acid by a method identical with that already employed to examine the transformation of pyrophosphoric acid into orthophosphoric acid, *i.e.*, by the

action of sulphuric acid (*Comptes Rendus*, vol. cxxxv., p. 961); (2), the heat of solution of solid metaphosphoric acid prepared by the calcination of PO_4H_3; (3), the heat of solution of fused sodium metaphosphate (Graham's soluble metaphosphate); (4), the heat of neutralisation of metaphosphoric acid by soda.

Certain Sources of Mineral Gases.—Ch. Moureu.—(See p. 38).

Cryoliths. — E. Baud. — The author prepares the hydrated sodium cryolith, the hydrated potassium cryolith, and the double ammonium fluoride, and in each case finds their heats of precipitation. He also examines the natural anhydrous cryoliths, and finds their heats of formation. The knowledge of the heat of formation of the sodium cryolith and that of anhydrous fluoride of aluminium is indispensable in the metallurgy of aluminium when it is necessary to calculate the quantity of electric energy necessary to decompose the cryolith.

A New Method of Estimating Hydroxylamine Volumetrically.—L. J. Simon.—The author believes that up to the present time there has been no satisfactory method of estimating hydroxylamine, and so he devises a volumetric estimation founded on the particular action of permanganate of potash on the oxalate of hydroxylamine. The latter is a well crystalline and anhydrous salt, which can easily be obtained in a pure state owing to its slight solubility in water. The action takes place in two phases, the first being expressed by the equation—

$$2MnO_2K+4[C_2O_4H_2(NH_2OH)] = \\ =2C_2O_4Mn+2C_2O_4KH+N_2O+6N+15H_2O,$$

and in the second phase in presence of sulphuric acid the oxalic acid is oxidised in the ordinary manner, evolving carbon dioxide. Very good results were obtained by this method.

Composition and Constitution of Sulphohydrated Hydrates.—M. de Forcrand.—In 1882 the author discovered a series of mixed hydrates to which he attributed the uniform composition $M+2H_2S+23H_2O$; M being a volatile halogenated organic compound analogous to the simple ethers of the fatty series. H_2S can also be replaced by H_2Se. He further develops this research, and proves that all these compounds are formed by the union of two simple hydrates, $(M+mH_2O)+2(H_2S+m'H_2O)$; m' being probably 6, since the formula of the simple hydrate of sulphuretted hydrogen is H_2S+6H_2O.

Metho-ethenylbenzene Di-bromide.—M. Tiffeneau.—Dibromomethoethenylphene, $C_6H_5—CBr(CH_3)—CH_2Br$, when acted upon by alcoholic KOH loses 1 molecule of HBr, giving the compound C_9H_9Br, which corresponds to one of the two formulæ:—(1) $C_6H_5—C(CH_2Br)=CH_2$, or (2) $C_6H_6—C(CH_3)=CHBr$; the second being proved the correct one on account of its action with Mg and Na. The author examines the properties of this substance.

Synthesis of a derived Aromatic Carbide of Camphor.—C. Chabrié.—By heating chloride of camphor with benzene and using many precautions, finally an oily liquid separates. Amongst the compounds contained in this liquid the author isolates an almost colourless substance, passing over at about 315°, and whose composition corresponds to the formula $C_{16}H_{18}$, and is formed according to the reaction $C_{10}H_{15}ClO+C_6H_6=C_{10}H_{13}.C_6H_5+H_2O+HCl$. He intends to further investigate this aromatic derivative of camphor and the other products formed at the same time.

Decomposition of certain Di- and Tribasic Organic Acids.—MM. Œchsner de Coninck and Raynaud.—The authors examine the decomposition products of malonic, succinic, tartaric, malic, and citric acids. The decomposition is effected methodically by heating them with glycol, glycerin, or sulphuric acid.

A Method of Transforming the Monochlorated and Monobromated Derivatives of the Hydrocarbons into Mono-iodated Derivatives.—F. Bodroux.—When small portions of iodine are added to an ethereal solution of a chloride and bromide of alcoyl-magnesium, the iodine rapidly disappears, and the solution becomes heated. The reaction takes place between a molecule of the organo-metallic compound and a molecule of iodine, a double salt of magnesium and an iodine derivative resulting, $\begin{matrix}R\\Br\end{matrix}>Mg+I_2=RI+Mg<\begin{matrix}I\\Br\end{matrix}$. The author applies this reaction to the aromatic series.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 11.

Estimation of Thallium in the Thallous State.—V. Thomas.—Already inserted.

Action of Bromine on Thallous Chloride in the presence of Water; Compounds of the Type Tl_2X_4.—V. Thomas.—Already inserted.

Chlorobromides of Thallium. Compounds of the Type Tl_4X_6.—V. Thomas.—Already inserted.

Action of Bromine on Thallous Chloride in the presence of Organic Solvents and in the Dry Way.—V. Thomas.—Already inserted.

Constitution of Tariric Acid.—A. Arnaud.—Already inserted.

The Nature and Properties of the Bodies formed in the Action of Chloroform on Naphthol β.—R. Fosse.—A long paper of 42 pages, mostly constitutional formulæ; unsuitable for abstraction.

Action of Hydroxylamine on some Halogen Derivatives of Methylphenylketone.—A. Collet.—The action of hydroxylamine on the halogen ketones gives halogen monoximes or dioximes, according to the conditions of the experiment. By using the method described by MM Korten and Scholl, the author has prepared the oximes of some other derivatives of methylphenylketone. He has also examined the action of hydroxylamine on a boiling alcoholic solution of the ω-monobromised and ω ω-dibromised derivatives of methyl-*p*-chlorophenylketone and of methyl-*p*-bromophenylketone; in these two cases he obtained the *p* chlorophenylglyoxime and the *p*-bromophenylglyoxime. The author has also prepared directly a certain number of the halogen-ketoximes, by reacting with the chlorides of chloracetyl and bromacetyl on para-chlorised or para-bromised aniline. The reaction is very lively, but can be made more quiet by diluting with sulphide of carbon. The products were purified by several crystallisations in boiling alcohol. They are in the form of colourless crystals, soluble in warm alcohol, but only slightly soluble in the cold; their fusing-points are:—

Chloracetanilide *p*-chlorised	167—168°
Chloracetanilide *p*-bromised	179—180°
Bromacetanilide *p*-chlorised	161°
Bromacetanilide *p*-bromised	168—169°

Crystallographic Properties of Benzylidene, Methyl and Ethylsalicylidene, and Anisal Camphors and their Products of Reduction.—J. Minguin.—The author gives the crystallographic properties of the above products and of some of their derivatives.

The Solubility of some Soft Resins.—Ch. Coffignier.—The resins were treated in two different manners; in one case 10 grms. of the resin were wrapped in Schleicher paper, and exhausted for five hours in a Soxhlet apparatus; in the second case 10 grms. of the resin were treated with 55 c.c. of a solvent for an hour at boiling-point, in a flask fitted with a vertical condenser; the insoluble portion was filtered off and washed with 100 c.c. of the solvent used. The details of the experiments made with various resins are given at length.

The Coefficient of Impurities of Brandies.—A. Cardoso-Pereira.—The results of numerous analyses made in the municipal laboratory of Paris show that commercial alcohols and wine-brandies have average coefficients of impurity of 0·0176 and 0·5184. Other

chemists have stated that the figure for wine-brandies is never lower than 0·300.

New Reducing Diastase extracted from Koji-japonais, and Secreted by "Eurotium Orizoe"; Jacquemose.—E. Pozzi-Escot.—This diastase, known by the name of "Koji" or "Taka," is met with commercially in two forms; the first, in tabloids, consists entirely of "Koji" or Japanese yeast; the second, in the form of an amorphous, yellow powder soluble in water, is "taka-diastase," or the active principle of Koji extracted by means of alcohol. The author has extracted a new diastase from Koji, having the same reducing power as *philothion*, but not possessing any hydrogenising properties with regard to sulphur; he proposes the name *reductase* for this series of products.

MISCELLANEOUS.

Preparation of Chlorine by means of Permanganates.—C. Graebe.—The author has experimented with both commercial and crystallised permanganate of potassium, as well as with permanganate of calcium, which is easily soluble. As a result of his experiments, he finds that when it is required to prepare small quantities of chlorine, the use of permanganate is very convenient, especially in cases where the presence of peroxide of chlorine would be objectionable; for its preparation on a large scale, the chlorate of soda method is preferable when the presence of the peroxide is not of importance. To prepare chlorine by means of permanganate, the same apparatus is used as with the chlorate of sodium method; solid permanganate is placed in a flask, and concentrated hydrochloric acid is dropped on to the salt very gradually. The operation is commenced in the cold, then heat is applied when half the necessary amount of hydrochloric acid has been added. To get off all the chlorine, it is necessary to use an excess of hydrochloric acid, and experience shows that about 10 molecules of acid are necessary for each 1 of permanganate instead of the 8 required theoretically. When the operation is properly carried out, almost the theoretical amount of chlorine is obtained.—*Berichte*, vol. xxxv., p. 13.

The Formation of Dithionic Acid.—J. Meyer.—The author explains the preparation of the dithionates in the following manner:—The action of SO_2 on MnO_2 does not at first produce either free dithionic acid or MnO, or sulphate of binoxide of manganese, but instead manganic sulphite (of the sesquioxide) and free oxygen; the manganic sulphite is then split up into dithionate and manganous sulphite—

$$2MnO_2+3SO_3H_2=(SO_3)_3Mn_2+3H_2O+O.$$
$$(SO_4)_3Mn_2=S_2O_6Mn+SO_3Mn.$$

In fact, he has observed analytically the presence of sulphite in the products of the reaction done in the cold. If this interpretation is correct, the hydrates of the sesquioxides (being able to form protoxides) of iron, cobalt, and nickel, suspended in water, and treated with a current of SO_2 at about 0°, ought to form first a sulphite of the sesqui-oxide, which will then decompose as above into hyposulphate and sulphite of the protoxide. Experiments have shown that this is the case. For instance, with $Fe_2(OH)_6$, we first obtain a deep red liquid (ferric sulphite), which soon becomes decolourised and gives a very good yield of dithionate. On the other hand, PbO_2 does not react on SO_2 in the presence of cold water; HgO is the same. As for the other binoxides, BaO_2, MgO_2, Na_2O_2, and H_2O_2, when treated with SO_2, they give H_2SO_4 directly in the cold. The examination and study of the electric conductivity and the cryoscopy of the solutions of dithionates, confirm the opinion that the molecule of dithionic acid is indeed $S_2O_6H_2$.—*Berichte*, vol. xxxiv., p. 3606.

MEETINGS FOR THE WEEK.

TUESDAY, 27th.—Royal Institution, 5. "The Physiology of Digestion," by Prof. Allan Macfadyen, M.D.

WEDNESDAY, 28th.—Society of Arts. 8. "The Cost of Municipal Trading," by Dixon H. Davies.

THURSDAY, 29th.—Royal Institution, 5. "Pre-Phœnician Writing in Crete, and its Bearings on the History of the Alphabet," by A. J. Evans, F.R.S.

FRIDAY, 30th.—Royal Institution, 9. "Vibration Problems in Engineering Science," Prof. W. E. Dalby.

SATURDAY, 31st.—Royal Institution, 3. "The Bi-centenary of Samuel Pepys—His Musical Contemporaries, Criticisms, and Compositions" (with Musical Illustrations), by Sir Frederick Bridge, M.V.O., Mus.Doc.

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FOR SALE.—"Nature," vols. 59 to 64. Also "Journal of the Society of Chemical Industry," 1898, 1899, 1900. Offers wanted.—Address, A. N., CHEMICAL NEWS Office, 16, Newcastle Street, Farringdon Street, London, E.C.

THE CHEMICAL NEWS.

VOL. LXXXVII., No. 2253.

REVISION OF THE ATOMIC WEIGHT OF LANTHANUM.*

By BOHUSLAV BRAUNER, Ph.D.,
and
FRANTIŠEK PAVLÍČEK,† Bohemian University, Prague.

THE atomic weight of lanthanum belongs to those constants which have been relatively often determined. It is seen from Table I., given below, that since the year 1842, twenty-six series of determinations have been made by fifteen chemists, whereas in the case of, for example, the technically important iron, we possess only seven determinations. But whereas the numbers obtained for iron are all approximate to 56, those obtained for lanthanum differ considerably from one another, the minimum being La=132·55 and the maxium La=148·25 (difference =15·7), and if we take into account only the most trustworthy determinations made within recent times, we have a minimum of 135·0 and a maximum of 139·7, the difference being 4·7.

In Table I., the first column contains the name of the chemist, and the numbers in brackets show that several determinations were made by the same chemist. The second column gives the date of publication, the third column indicates shortly the method used and the ratio from which the atomic weight was calculated. The last column gives the resulting "atomic numbers" with regard to O=16. The numbers were calculated from the data contained in the classical work of Clarke ("A Recalculation of the Atomic Weights," Revised Edition, Washington, 1897). With regard to O=16 and S=32·07, used by Clarke, on using the international S=32·06, which was used for the calculation of the results obtained in the present paper, the numbers of the table depending on the atomic weight of sulphur would be reduced by 0·02.

The last lines of the table contain the mean values, as calculated by different chemists, for their atomic weight tables.

The abnormally low number, La=135, which appears several times in the table, is not without some historical interest.

In 1870, Mendeléeff was of opinion that the quadrupled equivalent of lanthanum, $\frac{135}{3} \times 4 = 180$, represented its true atomic weight, and that the element belonged to the fourth group.

The determination of the specific heat of metallic lanthanum by Hillebrand, in 1874, proved that the order of the atomic weight of lanthanum is 138, but in spite of this Winkler, in 1891 (*Ber.*, xxiv., 889), considered that the composition of lanthanum hydride prepared by him is best represented by the simple formula LaH_2, if we assume $La^{IV}=180$.

I have shown (*Ber.*, 1891, xxiv., 1328) that the atomic weight of lanthanum cannot differ much from $La^{III}=138·2$, and that the hydride has the formula La_2H_3, which is analogous to that of the hydride of the quadrivalent cerium, Ce_2H_4. On examination of the spark spectrum of the fractions of lanthanum material yielding the apparent atomic numbers 132 to 135, I found that these low numbers are due to the admixture of yttrium (Y=89).

In 1898, on examining the solubilities of the oxalates of some rare earths in normal sulphuric acid, I found that that of yttrium appproaches that of lanthanum, so that on fractionating with oxalic acid certain lanthanum fractions may contain an admixture of yttrium.

Although it was thus proved by me that the low

* From the *Transactions of the Chemical Society*, 1902, vol. lxxxi.
† Read Pavleetchek.

TABLE I.—*Determinations of the Atomic Weight of Lanthanum.*

Chemist.	Date.	Method and ratio used.	La (O=16, S=32·07).
Rammelsberg	1842	$La_2(SO_4)_3 : 3BaSO_4$	132·55
Marignac (1)	1849	$La_2(SO_4)_3 : 3BaSO_4$ (A)	139·53
Marignac (2)	1849	$La_2(SO_4)_3 : 3BaSO_4$ (B)	148·25
Marignac (3)	1849	$La_2(SO_4)_3 : 3BaCl_2$	141·27
Holzmann (1)	1858	$La_2O_3 : 3BaSO_4$	139·46
Holzmann (2)	1858	La_2O_3 in $La_2(IO_3)_6,3H_2O$	137·59
Holzmann 3)	1858	La_2O_3 in $La_2Mg_3(NO_3)_{12},24H_2O$	138·68
Czudnowicz	1860	$La_2O_3 : 3BaSO_4$	133·00
Hermann (1)	1861	$LaCl_3 : Cl_3$	139·25
Hermann (2)	1861	$La_2(SO_4)_3 : La_2O_3$	139·52
Hermann (3)	1861	$La_2O_3 : 3CO_2$	139·36
Zschiesche	1868	$La_2(SO_4)_3 : La_2O_3$	135·35
Erk (1)	1871	$La_2(SO_4)_3 : La_2O_3$	135·65
Erk (2)	1871	$La_2(SO_4)_3 : 3BaSO_4$	134·79
Marignac (4)	1873	$La_2(SO_4)_3 : La_2O_3$	138·81
Cleve (1)	1874	$La_2O_3 : La_2(SO_4)_3$	139·29
Brauner (1)	1882	$La_2O_3 : La_2(SO_4)_3$	138·88
Brauner (2)	1882	$La_2O_3 : La_2(SO_4)_3$	138·36
Cleve (2)	1883	$La_2O_3 : La_2(SO_4)_3$	138·36
Bauer	1884	$La_2O_3 : La_2(SO_4)_3$	138·77
Bettendorff	1892	$La_2O_3 : La_2(SO_4)_3$	138·71
Gibbs and Shapleigh	1893	$La_2O_3 : 3C_2O_3$ and $La_2O_3 : La_2(SO_4)_3$	139·71
Schützenberger	1895	$La_2O_3 : La_2(SO_4)_3$. Principal fraction	138·0
Schützenberger	1895	$La_2O_3 : La_2(SO_4)_3$. Side fraction	135
Muthmann	1899	?	138·4 ?
Atomic Weight Tables—			
Clarke	1897	"Recalculation," mean	138·64
Clarke	1897	Cleve's and Brauner's numbers only	138·36
Clarke	1901, 1902	American Commission Reports for 1900, 1901	138·6
International	1902	German Chemical Society Commission	138
Richards	1901	Own table	138·5

numbers of about 135, obtained for the atomic weight of lanthanum, are due to an admixture of yttrium, this abnormal value reappeared once more in chemical literature. Schützenberger, in 1895 (*Comptes Rendus*, cxx., 1143), found that some fractions of lanthanum contained the ordinary lanthanum, La=138, others a second lanthanum with the atomic weight La=135. This lower number is regarded by Rydberg (*Zeit. Anorg. Chem.*, 1897, xiv., 99) as the real atomic weight of lanthanum, as, according to his view, it agrees better with certain numerical relations observed by him in atomic numbers.

The objects of the present work were :—

(1) To ascertain whether the purest lanthanum preparations, that is, those corresponding with the *most basic* of all cerite earths, are homogeneous, and what is the real atomic weight of the element contained in them.

(2) To determine whether the atomic weight of lanthanum is somewhat higher than 138·4, for, according to the "twin rule" of Lorenz (*Zeit. Anorg. Chem.*, 1895, xii., 329), it ought to approach the number La=139.

In this connection, it may be pointed out that if the number C=139·0, calculated from the determinations of Wyrouboff and Verneuil (*Bull. Soc. Chim.*, 1897, [3], xvii., 679), by Clarke (*Annual Report of the Committee of Atomic Weights*, 1897), for the atomic weight of cerium, be correct, we should expect the atomic weight of lanthanum to be considerably lower than La=139.

(3) To investigate once again the question whether or no, in ordinary lanthanum free from yttrium, fractions are contained the element of which possesses an atomic weight of 135.

(4) To discover whether the classical method used for the determination of the atomic weights of almost all rare earth elements, that is, the conversion of the oxide into the sulphate, contains any hidden source of error.

Preparation of Material.

In 1873 (*Annalen*, clxviii., 45), a new method was described by Mendeléeff for the easy separation of lanthanum from didymium. It consists in re-crystallising the double nitrates with ammonium nitrate from an aqueous solution.

This method was modified by Auer von Welsbach, in 1885 (*Monatsh.*, vi., 491), who did not quote Mendeléeff, and is therefore wrongly regarded as the originator of the method, by re-crystallising the double nitrates in the presence of nitric acid. At the end of his paper, in which the separation of the old didymium into "neodym" and "praseodym" (the latter separates with lanthanum) is described, this author says that lanthanum, like his "twin" didymium, will sooner or later disappear from the series of elements, a statement which means that, in his opinion, it consists of a mixture of elements.

This fact was observed by me previously, in 1882 (*Monatsh.*, iii., 176). A most "negative" fraction was obtained from lanthanum with an "atomic weight" of $R^{III}=140{\cdot}19$, and in the spark spectrum, in which the yttrium lines were prominent, some lines belonging neither to lanthanum nor to yttrium were observed.

Mendeléeff's method, as modified by Auer, was employed for the purification of the lanthanum material used by Bettendorff in 1892, as well as by Gibbs and Shapleigh in 1893 in their atomic weight determinations (see Table I.). Quite recently, Melikoff and Pissarjewsky (*Zeit. Anorg. Chem.*, 1899, xxi., 70), without knowing that they return to Mendeléeff's original method, recommend re-crystallisation from the *neutral* solution for the preparation of pure lanthanum compounds.

Many years ago, fractional precipitation with magnesia was recommended for the above purpose by Stolba. Drossbach (*Ber.*, 1896, xxix., 2452) used it for the separation of the yttrium earths. Without quoting their predecessors, Muthmann and Rölig (*Ber.*, 1898, xxxi., 1718) recommend it for the *easy* and *rapid* preparation of *pure* lanthanum compounds, and they obtain from 470 grms. of the crude oxide mixture 200 grms. of *perfectly pure* lanthanum oxide. However, in a paper by Ley (*Zeit. Physikal. Chem.*, 1899, xxx., 236), we find in a footnote the surprising statement that Muthmann and Rölig's material was in reality far from being pure, and contained yttria earths. Its original atomic weight was $R^{III}=139{\cdot}5$ and after fractionation a less basic portion with an atomic weight of $R^{III}=140{\cdot}1$ and a more basic portion with an atomic weight La=138·4 *are said* to have been obtained.

The material which was used for the preparation of lanthanum compounds for the purpose of the present investigation was obtained from cerite. Since the year 1885, much time has been devoted by me and by some of my advanced students to the fractional crystallisation of a considerable quantity of the double ammonium nitrates of a crude mixture of lanthanum and old didymium free from cerium by the Mendeléeff-Auer method. After a long series of crystallisations, lanthanum was obtained free from praseodym, neodym, and the whole of the elements of the samarium, gadolinium, and yttrium group.

For the further purification, a *second method* was used consisting in the fractional fusion of the lanthanum nitrate thus obtained with a mixture of potassium and sodium nitrates in molecular proportion (Debray-Schützenberger method). A trace of cerium and of the less basic earths was removed first by fusing for half a day at 350°; the mass was dissolved in water, filtered, and the residue washed with a saturated solution of the alkali nitrates in water in order to avoid the finely divided oxides passing into the filtrate.

The filtrate from this fraction, A1, was carefully evaporated down and the moist residue obtained had to be dried very carefully before fusion, a tedious operation requiring a great deal of time.

On repeating the fusion, &c., first at 450—500° and for the last fractions even at a higher temperature, the fractions A2, A3, A4, A5, and A6 were obtained. They consisted of basic lanthanum nitrate and were perfectly white.

A *third method* of fractionation was used for the further purification of the highly purified lanthanum material, A6, which did not contain the slightest trace of an yttria earth or of an earth yielding an absorption spectrum. Instead of using such weak bases as ammonia or magnesia, or of following Drossbach, who used sodium hydroxide, we used the most powerful base available, namely, potassium hydroxide, which precipitates lanthanum as the hydroxide. The latter, on being digested with a hot solution of, for example, lanthanum nitrate, is converted into the basic nitrate, and in such a precipitate the *least basic* portion contained in the solution is accumulated, whereas the most basic or positive portion passes into the solution. In this way, lanthanum solutions are precipitated by lanthanum hydroxide.

The method of fractionation differed in one essential point from similar methods hitherto used, for instead of precipitating *small* fractions and leaving the greater part in solution, the *larger* part was precipitated, leaving only the *smaller* part in solution—this considered to be the fraction sought.

After calculating from a preliminary experiment the volume of a definite dilute solution of potassium hydroxide necessary for the *complete* precipitation of lanthanum, sufficient was added to the main solution to precipitate seven-eighths and to leave one-eighth in solution. The addition was made drop by drop from a large burette and the precipitate digested for some time with the solution and then filtered.

After dissolving the precipitate in the smallest amount of dilute nitric acid, and repeating the above process of fractionation, the following eight fractions were obtained :—La0, La1, La2, La3, La4, La5, La6, La7. If lanthana is a mixture of earths, the lower fractions must contain the most basic (positive) portion, whereas the least basic (negative) portion will be accumulated in the highest fraction.

The solutions containing the above fractions were first completely precipitated by potash, the washed precipitate was dissolved in an insufficient quantity of dilute nitric acid, which was added drop by drop with stirring, and the solution filtered from a small, insoluble residue consisting chiefly of silica and other negative impurities.

After this, recourse was had to repeated precipitation with ammonia and washing of the precipitate in order to remove the alkalis completely. From the nitric acid solution of the last precipitate, lanthanum oxalate was in each case precipitated by adding a dilute solution of sublimed oxalic acid drop by drop. The crystalline, white, and fine powder of the precipitate was well washed with water, but as the mode of washing has a great influence on the *composition* of the oxalate, this point will be more fully treated in a subsequent section.

Method of the Atomic Weight Determination.

It has been generally considered that the most simple and trustworthy method for the determination of the atomic weight of the element of a rare earth is the conversion of the oxide R_2O_3 into the sulphate $R_2(SO_4)_3$.

Bunsen dissolved the oxide in dilute sulphuric acid and removed the excess by evaporation, but as the reaction is an exothermic one, and the sulphates are only slightly soluble at a low, and still less so at a higher, temperature, some solid sulphate may separate out before the oxide has dissolved completely.

In order to avoid the error due to incomplete solution in sulphuric acid, the oxide is now generally dissolved in nitric acid, after which dilute sulphuric acid is added and the excess of the acids removed by evaporation.

In chemical literature, very vague and incomplete indications are found regarding the temperature at which the excess of sulphuric acid is removed from the sulphate. Although sulphuric acid boils at 338°, a much higher temperature than this is recommended for its removal, and the sulphate is generally heated for some time at, or a little above, 400° in order to remove all free sulphuric acid.

The only chemist who has directed his attention to the question of the equilibrium between the basic and acid constituents of the sulphate of a rare earth is Bailey (*Trans.*, 1887, li., 683). On heating "didymium" sulphate containing an excess of sulphuric acid slowly to and above 360° he could not find any range of temperature within which the weight of the salt would remain perfectly constant. Each increase in temperature led to a further loss of weight and an equilibrium could not be obtained. Bailey says that it remains to be seen whether the other earths of this group show similar variations.

It should be added that a means of ascertaining whether the sulphate obtained by synthesis is normal was proposed by Cleve, Nilson, and others: it must dissolve in water without leaving an insoluble residue of the basic sulphate. This test only shows whether *too much* sulphuric acid has been removed, and yet we shall see that this criterion is not trustworthy. No one, however, has considered the other side of the question: How can we find out whether the sulphate does not contain an *excess* of sulphuric acid?

In the experiments recorded in this paper, we proceeded as follows. Air-dried lanthanum oxalate was heated gradually and carefully until the oxide was obtained. This was heated in a double platinum crucible* to the highest yellow heat in a strongly oxidising flame.

The oxide obtained from the fractions La0, La1, La2, La3, and La4 was at first perfectly white, but on being heated for a longer time the part in contact with the hot walls of the platinum crucible assumed an extremely slight pale buff tint. This tint was slightly more prominent in the higher fractions, especially in La7.

Lanthanum oxide, which was weighed after cooling over phosphoric oxide, was slowly and carefully dissolved in water to which nitric acid was added very gradually, after which a small excess of dilute sulphuric acid of known strength was added. A blank experiment made with the quantities used (5—10 c.c. of water, 2 c.c. of nitric acid, and 3 c.c. of sulphuric acid) showed that the residue obtained on evaporation in the air and after heating at 500° is inappreciably small.

After evaporation to dryness, the platinum crucible was fastened in the centre of a large porcelain crucible having in its lid a thermometer graduated up to 550°, by which at least the order of the temperature was indicated. The large crucible fitted into a larger plate of asbestos cardboard in order to exclude the products of the combustion of coal gas (chiefly water and carbon dioxide) from the atmosphere of the crucible.

Experiment I.—0·97175 grm. La_2O_3 was converted as above into the sulphate, and the latter containing an excess of sulphuric acid was heated in the crucible air-bath.

Time of heating.	Temperature.	Weight of sulphate in grms.	"Atomic Weight" of La.
3 hours	350° ±	1·7112	133·70
5 ,,		1·7025	133·52
5 ,,		1·6990	136 28
6 ,,		1·6982	136·48
5 ,, (total 24 hours)		1·6982 constant	136·48
3 ,,	450° ±	1·6978	136·56
6 ,,		1·6955	137 06
6 ,,		1 6949	137·20
4 ,, (total 19 hours)		1·6938 constant	137·45
Direct flame in hand	—	1·6935	137 41
below red heat		1·6930	137·62

It is seen from this experiment how slowly and incompletely the excess of sulphuric acid is driven off, and it will be seen later on that it cannot be driven off completely unless the substance be heated 200—300° above the boiling point of the acid.

This behaviour is undoubtedly due to the presence of an acid sulphate of lanthanum analogous to the acid sulphate of cerium described by Wyrouboff (*Bull. Soc. Chim.*, 1890, [3], ii., 275). The vapour pressure of sulphuric acid in this salt must be smaller than that of the free sulphuric acid. The partial formation of this salt was confirmed by our experiments.*

Lanthanum sulphate, obtained in Experiment I., was dissolved in water, and the solution was found to be *strongly acid* towards ethyl-orange. But first the question had to be considered whether and how far normal lanthanum sulphate is hydrolysed in aqueous solution.

Ley (*Zeit. Physikal. Chem.*, 1899, xxx., 236) found by physical methods that salts of lanthanum with strong acids are only very slightly hydrolysed at the ordinary temperature, so that, for example, lanthanum chloride in aqueous solution shows, in the presence of phenolphthalein, a very slightly acid reaction, but he says nothing about the sulphate.

* The proposal to heat the platinum crucible (with the substance) which is to be weighed inside another platinum crucible was made by my former teacher, Prof. Stolba, some thirty years ago. The inner crucible does not come into contact with the flame gases, and does not change its weight. Its surface does not become rough by crystallisation, or from little sand and dust particles which, being projected on the soft, white-hot metal, stick to it and make it often heavier. I have used the same crucibles for the last twenty years, and they look like new to-day, and, what is more important, *they do not leak*, whereas crucibles which are heated *directly over the blast* invariably do so after a few months' use, so that they become unfit for any kind of exact work.

* In order to avoid the mere assumption of the existence of a hypothetical acid sulphate of lanthanum, I asked Mr. Picek to prepare it. He succeeded in doing so by a novel method, differing from that used by Wyrouboff. The result of this work was the preparation of a whole series of acid sulphates in a pure state possessing the general formula $R^{III}_2(SO_4)_3{,}3H_2SO_4$, in which R^{III}=Ce, La, Pr, Nd, Y, and Sm. This fact was communicated to the Chemical Society on February 24, 1902. As the acid sulphates of Pr and Nd were described several weeks later by Matignon (*Compt. Rend.*, 1902, cxxxiv., 657), I am obliged to make this statement in order to prove that our discovery was made independently of that of Matignon.

Behaviour of Lanthanum Sulphate towards Ethyl-orange.

A larger portion of lanthanum oxide from the fraction A5+6 was converted into the sulphate with all due precautions, and this was heated for a long time to incipient redness in order to remove the excess of sulphuric acid as far as possible. It was dissolved in 6 parts of ice-cold water. One part of this solution was heated to 35—40°; the hydrated salt which separated out was collected on a perforated platinum plate with the aid of a pump and well washed with water. From another part of the solution, the salt was precipitated with alcohol, collected at the pump, and well washed. The salt prepared by either method was heated in the crucible air-bath for a long time at about 550°, and 1 grm. of the anhydrous substance dissolved in 50 grms. of water.

On addition of 5 drops of a dilute (1 : 500) alcoholic solution of *our* ethyl-orange, which was found to be more sensitive as regards the transition near the neutral point than *our* methyl-orange, the above *standard* solution of lanthanum sulphate was found to be very nearly neutral; it exhibited, however, a slight but distinct orange tint as compared with the same quantity of water containing the same quantity (5 drops) of ethyl-orange which was more yellow, so that it would seem that it is *very slightly* hydrolysed in aqueous solution.

In all atomic weight determinations recorded below, the lanthanum sulphate was dissolved in 50 parts of water, and after addition of 5 drops of our ethyl-orange these solutions were titrated with N/20 to N/30 solution of sodium hydroxide (sometimes a N-20 solution of sulphuric acid was also used, and the titration was done to and fro) until the above "standard" tint was reached. The volume of the alkali used was reduced to the corresponding volume of the N/10 solution and every c.c. multiplied by 0·0049038. The weight of sulphuric acid obtained is then subtracted from that of the weight of the "*crude*" sulphate.

As it was found in several preliminary experiments, not recorded here, that the synthetical lanthanum sulphate, which was heated at about 500°, was rather strongly acid, so that the correction determined acidimetrically would be rather large, we tried to diminish it by heating the salt at about 550° in an atmosphere of ammonia. For this purpose, ammonium carbonate was projected upon the red-hot bottom of the porcelain crucible containing in its centre the open platinum crucible, after which the lid of the porcelain crucible was replaced immediately. After several repetitions of this process, the sulphate obtained was far less acid, and even sometimes *neutral* or *normal*, as regards the aqueous solution finally obtained.

Lanthanum sulphate, obtained by evaporation of its nitric acid solution, forms a loose mass of fine needles. On heating the salt to a temperature which in some cases may have finally exceeded 600°, that part which adheres to the platinum walls of the crucible may become partly converted into the *basic* salt, that part which lies nearer the centre may consist of the *normal* salt, and the uppermost inner layer may consist of some incompletely decomposed *acid* sulphate. On dissolving such a mixture in water tinted with ethyl-orange, the salt at first rapidly dissolves with an acid reaction, then the solution proceeds more slowly, the acid reaction diminishes, and the last insoluble portion containing the basic salt is brought into solution slowly but completely by the free sulphuric acid resulting from the hydrolysis of the acid sulphate. It is a matter of mere chance that in some experiments the aqueous solution of the sulphate resulting after the above equilibrium had taken place was neutral. In other cases it was acid.

In none of the 27 experiments recorded in this paper was the solid lanthanum sulphate prepared by synthesis homogeneously neutral or homogeneous in all its parts. This is due to the circumstance that it hitherto has been found impossible to heat the system: crucible + sulphate, throughout exactly *to the same temperature.*

The above process may be called one of "self neutralisation." If it takes place according to an equation such as this—

$$3[La_2O_3,2SO_3]+La_2O_3,3SO_3,3H_2SO_4+Aq=$$
$$=4[La_2O_3,3SO_3]+3H_2O+Aq$$

it is seen that some water is set free, but no account can be taken of its quantity in the final calculation of the atomic weight. However small this unknown factor may be, it tends to make the atomic weight lower than the true number.

It is seen from the above that the criterion proposed by Cleve and others for the test of normality of the sulphate obtained by synthesis does not hold good, for we are not entitled to reject the results of those experiments in which the sulphate does not dissolve in water at once but only after some time.

(To be continued).

ON THE DETERMINATION OF LEAD IN ORES.*

By IRVING C. BULL.

(Continued from p. 44).

G. *Dichromate Method.*

POPE'S method consisted in converting the lead to lead sulphate and then to acetate, adding an excess of potassium dichromate, destroying the excess with standard arsenic trioxide solution, and titrating the excess with standard iodine solution and starch paste as indicator. This method seemed to require at a glance too much manipulation, so was not tried.

J. H. Wainwright's method is to precipitate the chromate as usual from an acetate solution, and the end noted by a silver nitrate solution giving a red-spot test on a white porcelain plate. This was found to be so inaccurate and troublesome, even on standardising a dichromate solution with a known strength lead acetate solution, that the method was not executed; high results would be always obtained, the cause being that the end point is obscured by the yellow lead chromate which reacts with the silver nitrate; this may, however, be somewhat overcome by boiling the solution hard after each addition of potassium dichromate, and allowing to settle.

Sutton's back titration was carried out as follows:—Follow out the gravimetric lead sulphate method through the point where the lead sulphate is dissolved in ammonium acetate. Dilute this acetate solution to about 150 c.c. and boil, run in a sufficient amount of a standard solution of potassium dichromate to precipitate all the lead and about one-third as much again in excess, boil hard for two minutes, filter quickly on a Gooch crucible, and wash thoroughly with hot water until there is no yellow colour to the wash water, dilute the filtrate to 400 c.c., and titrate with standard solution of ammonium ferrous sulphate at 60° C., after acidifying the solution with about 15 c.c. of dilute hydrochloric acid or 5 c.c of concentrated sulphuric acid. The end point is noted by a dark blue colour produced when a drop of the titrated solution is added to a drop of potassium ferricyanide upon a white porcelain plate.

This excess of dichromate may also be determined by adding 3 or 4 grms. of potassium iodide to the solution, keeping it about 600 c.c. bulk and normal temperature, 15 c.c. of concentrated sulphuric acid added, and the liberated iodine titrated with a standard sodium hyposulphite solution, adding the latter until nearly to the end, then just before the end point is reached add two or three drops or

* Contribution from the Havemeyer Laboratories, Columbia University. From the *School of Mines Quarterly*, xxiii., No. 4.

c.c. of a freshly prepared solution of starch paste, and the end point noted by the disappearance of the blue colour.

The following results were obtained upon the ores, using both titrations, which agree fairly well:—

	Ferrous.		"*Hypo.*"	
.. ..	78·71 per cent	1	78·71 per cent	
	78·78 ,,		78·76 ,,	
2	37·32 ,,		78 73 ,,	
	37·28 ,,	2	37·33 ,,	
3	10·78 ,,		37·34 ,,	
	10·72 ,,		37·37 ,,	
4	18·48 ,,	3	10·80 ,,	
	18 44 ,,		10·76 ,,	
5	27·31 ,,		10·81 ,,	
	27·27 ,,	4	18·50 ,,	
6	38·46 ,,		18·45 ,,	
	38·52 ,,	5	27·26 ,,	
			27·32 ,,	
		6	38·57 ,,	
			38·60 ,,	
			38·56 ,,	

The results obtained by making weighed additions of impurities, using the ferrous titrations, were as follows:—

Bismuth.

					K dichromate sol.
1. 30 c.c.	PbA sol.	2·5 c.c.	Bi nitrate sol.		19·30 c.c.
2. 30 ,,	,,	5 ,,	,,	,,	20·09 ,,
3. 30 ,,	,,	10 ,,	,,	,,	21·60 ,,
4. 30 ,,	,,	20 ,,	,,	,,	26·44 ,,
5. 30 ,,	,,	40 ,,	,,	,,	34·20 ,,

Antimony.

1. 30 c.c.	PbA sol.	0·0 c.c.	Sb chloride sol.		18·60 c.c.
2. 30 ,,	,,	2·5 ,,	,,	,,	19·40 ,,
3. 30 ,,	,,	5 ,,	,,	,,	21·10 ,,
4. 30 ,,	,,	10 ,,	,,	,,	21·66 ,,
5. 30 ,,	,,	20 ,,	,,	,,	24·80 ,,

Barium.

1. 30 c.c.	PbA sol.	2·5 c.c.	Ba chloride sol.		19·81 c.c.
2. 30 ,,	,,	5 ,,	,,	,,	20·83 ,,
3. 30 ,,	,,	10 ,,	,,	,,	22·80 ,,
4. 30 ,,	,,	20 ,,	,,	,,	24·64 ,,
5. 30 ,,	,,	40 ,,	,,	,,	28·30 ,,

Strontium.

1. 30 c.c.	PbA sol.	2·5 c.c.	Sr chloride sol.		18·90 c.c.
2. 30 ,,	,,	5 ,,	,,	,,	19·20 ,,
3. 30 ,,	,,	10 ,,	,,	,,	19·93 ,,
4. 30 ,,	,,	20 ,,	,,	,,	21·00 ,,
5. 30 ,,	,,	40 ,,	,,	,,	21·88 ,,

Calcium.

1. 30 c.c.	PbA sol.	2·5 c.c.	Ca chloride sol.		18·70 c.c.
2. 30 ,,	,,	5 ,,	,,	,,	18·76 ,,
3. 30 ,,	,,	10 ,,	,,	,,	19·34 ,,
4. 30 ,,	,,	20 ,,	,,	,,	20·20 ,,
5. 30 ,,	,,	40 ,,	,,	,,	21·50 ,,

In the above titrations the back titration with the ferrous solution has not been recorded, but the number of c.c. of the potassium dichromate actually required is given.

H. *Ferrocyanide Method.*

This method was first described by Low in the Chemical News for 1897, but on account of the lack of proper conditions the method proved somewhat erroneous. The method here pursued was as follows:—The lead sulphate was obtained as described in the gravimetric lead sulphate method. Add 10 c.c. of a cold saturated solution of commercial ammonium carbonate, and heat gently to boiling to prevent spattering, the heating being necessary to ensure the complete conversion of any sulphate of calcium to carbonate. Cool to ordinary temperature, and filter through the original filter, washing the precipitate, and flask thoroughly with cold water until no alkaline reaction is noted. Place in the flask about 5 c.c. of glacial acetic acid and 25 c.c. of distilled water and heat, place in this solution when hot the filter and precipitate of lead carbonate. Boil this until the lead carbonate is completely dissolved, dilute to about 150 c.c., heat to about 60° C., and titrate with a standard solution of potassium ferrocyanide, the end point being noted by the usual brown colour when a drop of the solution is placed on a white porcelain plate with a drop of saturated neutral solution of uranium acetate.

Beebe also describes a method similar in principle to the above in the Chemical News for 1896.

Free ammonia must be absent in the above described method, as it reacts with the uranium, interfering with the true colour, and so giving very low results. This colouration due to ammonia does not appear at once, but comes quickly as more ferrocyanide is added. Other indicators were tried, as platinic chloride; this was not affected by the salts in solution, but did not give a very sharp end reaction, so is not recommended; nitrate of cobalt was even less satisfactory.

The conditions best adapted for the titration, found by many experiments, were:—Bulk of solution to be titrated should be as near as possible to 100 c.c. containing about 10 c.c. of 50 per cent acetic acid, temperature about 60° C.; the correction for the indicator is then about eight-tenths of 1 c.c. These are the most convenient conditions to maintain and which will give the lowest allowance for the indicator. A 1 per cent potassium ferrocyanide was used. It cannot be over-emphasised that it is very important to always maintain these conditions, as a slight variation gives erroneous results on account of the variation in the composition of the precipitate.

The effect of impurities upon the method was as follows, being carried out in the usual way as before described:—

Antimony.

					K ferrocyanide sol.
1. 30 c.c.	PbA sol.	0·0 c.c.	Sb chloride sol.		35·40 c.c.
2. 30 ,,	,,	2·5 ,,	,,	,,	35·35 ,,
3. 30 ,,	,,	5 ,,	,,	,,	35·40 ,,
4. 30 ,,	,,	10 ,,	,,	,,	35·38 ,,
5. 30 ,,	,,	20 ,,	,,	,,	35·40 ,,

Bismuth.

1. 30 c.c.	PbA sol.	2·5 c.c.	Bi nitrate sol.		35·40 c.c.
2. 30 ,,	,,	5 ,,	,,	,,	35·30 ,,
3. 30 ,,	,,	10 ,,	,,	,,	35·10 ,,
4. 30 ,,	,,	20 ,,	,,	,,	35·00 ,,
5. 30 ,,	,,	40 ,,	,,	,,	34·80 ,,

Barium.

1. 30 c.c.	PbA sol.	2·5 c.c.	Ba chloride sol.		35·30 c.c.
2. 30 ,,	,,	5 ,,	,,	,,	35·20 ,,
3. 30 ,,	,,	10 ,,	,,	,,	34·98 ,,
4. 30 ,,	,,	20 ,,	,,	,,	34·85 ,,
5. 30 ,,	,,	40 ,,	,,	,,	33·80 ,,

Calcium.

1. 30 c.c.	PbA sol.	2·5 c.c.	Ca chloride sol.		35·40 c.c.
2. 30 ,,	,,	5 ,,	,,	,,	35·40 ,,
3. 30 ,,	,,	10 ,,	,,	,,	35·35 ,,
4. 30 ,,	,,	20 ,,	,,	,,	35·40 ,,
5. 30 ,,	,,	40 ,,	,,	,,	35·38 ,,

Strontium.

1. 30 c.c.	PbA sol.	2·5 c.c.	Sr chloride sol.		35·40 c.c.
2. 30 ,,	,,	5 ,,	,,	,,	35·40 ,,
3. 30 ,,	,,	10 ,,	,,	,,	35·42 ,,
4. 30 ,,	,,	20 ,,	,,	,,	35·38 ,,
5. 30 ,,	,,	40 ,,	,,	,,	35·40 ,,

The following results were obtained on analysis of the six ores.

1.	78·67	per cent
	78 65	,,
2.	37·31	,,
	37·29	,,
3.	10·90	,,
	10·86	,,
4.	18·44	,,
	18·48	,,
5.	27·25	,,
	27·18	,,
6.	38·65	,,
	38·58	,,

(To be continued).

ESTIMATION OF GLYCERIN BY MEANS OF IODIC ACID IN THE PRESENCE OF SULPHURIC ACID.

By A. CHAUMEIL.

The methods now in use for the estimation of glycerin are fairly numerous, and we have no intention of recapitulating them here. Some are so difficult of execution that they have been abandoned, while others have been dropped owing to their want of accuracy.

All the methods, however, can be divided into two groups:—

1. The ponderable methods, for the estimation of glycerin in fermenting liquors of saccharine origin (wine, beer, cider).

2. The volumetric methods, applicable to glycerins of industrial origin (soap and stearin works).

M. G. Demoussy who has studied the question carefully says ("Dictionaire de Würtz," Suppl., vol. iv., Art. "Glycerin"):—"The only method which, up to the present, appears satisfactory all round is the bichromate of potassium method, and we are of the opinion that all estimations of glycerin, without exception, should be made by means of bichromate; that is, until a more simple and more exact method has been discovered."

The method just referred to offers certain difficulties which we have endeavoured to obviate by substituting for the bichromate of potassium a much more energetic oxidising agent, viz., *iodic acid*, which has the great advantage over bichromate of potassium of not being decomposed by sulphuric acid, no matter how concentrated the latter may be.

The action of iodic acid on organic matters has been made clear by the researches of M. H. Causse; according to the nature of the substance, or rather its constitution, it is sometimes attacked directly, as in the case of uric acid or morphine; or its attack necessitates the intervention of sulphuric acid in variable quantities. All these facts have been the subject of several papers by MM. Gallimard, Bouillet, and Romeyer.

Following the advice of M. Causse I undertook a series of experiments which have led to the method I am about to describe.

Principle of the Method.

When iodic acid is placed in contact with glycerin, the latter is decomposed, carbonic acid is formed, and iodine is set free; however, under these conditions the attack is decidedly incomplete, but if we add sulphuric acid, the combustion of the glycerin is integral, and may be represented then by the following equation:—

$$5C_3H_8O_3+7I_2O_5=15CO_2+20H_2O+7I_2,$$

from which it follows that 5 molecules of glycerin, or 460 of the polyalcohol, liberate 7 molecules of iodine or 1778 of the metalloid.

Thus one part of iodine corresponds to 0·2587 grm. of glycerin; let V be the volume of decinormal hyposulphite of soda used to estimate the iodine set free, and of which 1 c.c. corresponds to 0·0127 grm. of iodine; the glycerin $=V\times0{\cdot}0127\times0{\cdot}2587$.

Before going into details of the operation we will take two typical cases like M. Demoussy, viz., the glycerin contains substances like chloride of sodium capable of acting on iodic acid, or it does not.

First Case:—The Glycerin is Free from Substances Acting on Iodic Acid.

The solutions necessary for making an estimation are:—A solution of iodic acid at one-fifth, and a decinormal solution of hyposulphite of sodium.

The apparatus we used is the same as that used by Mohr for the estimation of iodine.

Details of the Operation.

Into a tared crucible we pour a certain quantity, about 10 grms. of glycerin, and find its weight; dissolve in distilled water, and make the volume up to a litre. Place 10 c.c. of this solution in the flask, and add successively 25 c.c. of the iodic acid solution, 50 c.c. of sulphuric acid, and a fragment of marble. The flask is closed by means of the bulb-tube, and the condensing apparatus is plunged into a refrigerating vessel and furnished with iodide of potassium at one-fifth; the distillation is commenced, the iodine is given off, and dissolves in the iodide; at the same time the liquor in the flask becomes decolorised, though it still retains a pale yellow tint. This is due to the presence of a large quantity of sulphuric acid; it is probable that sulphuric ethers are formed from the glycerin which resists the attack of the iodic acid. Allow to cool for an instant, and add 25 c.c. of water; the liquid is again coloured, and a second distillation is made after having renewed the iodide in the condenser. When the contents of the flask are completely decolorised it is allowed to cool again, and we make sure that the combustion of the glycerin is complete by adding another 25 c.c. of water. Generally we obtain a slight colouration which corresponds to a few m.grms. of iodine, and which must be driven off into the iodide by distillation. There only remains now to add together the condensed liquids and titrate with decinormal hyposulphite.

Remarks.

Experience has shown us that three additions of water, under the given conditions, are necessary and sufficient to effect the combustion of the glycerin. Its *rôle* is easy to understand; it saponifies the sulphuric ethers of the glycerin, and the latter is set free and then oxidised by the iodic acid. The use of marble facilitates the operation in a remarkable manner; the carbonic acid which is given off maintains a slight pressure in the apparatus, and prevents the absorptions which are often so fatal in this class of estimation, especially at the end of the operation; but in such a case it is necessary to use a much longer condenser tube to make certain of the condensation of the iodine.

	Wt. of glycerin in 10 c.c. of solution. Grm.	Volume of N/10 hyposulphite used. C c.	Glycerin by the iodic acid method.	Glycerin by the bichromate method.	Results, per cent. Iodic acid method.	Results, per cent. Bichromate method.
10 c.c. = 0·0916		27·4	0·09002	0·08793	98·27	94·9
10 c.c. = 0·1154		34·8	0·115316	0·12398	99·90	107·1
10 c.c. = 0 08097 (commercial glycerin) ..		23·0	0·075566	0·06395	93·32	79·0

In the above table we give the results obtained both with the bichromate method and by the method we have just described; the operations were carried out on the same solution.

Second Case:—The Glycerin contains Chlorides.

We have mentioned above that for this particular case M. Demoussy recommends the elimination of the chlorides by a preliminary treatment with carbonate of silver.

Table Summing-up the Results of the Different Estimations of Glycerins by Iodic Acid.

Weight of glycerin at 30° B. in the sample.	Volume of N/10 solution of hyposulphite used.	Glycerin found.	Results per cent of material.
			Per cent.
Glycerin free from Chlorides.			
10 c.c. = 0·10 grm. glycerin	28·5 c.c.	0·09363	93·63
10 c.c. = 0·15886 ,, ,, ...	47·3 ,,	0·15608	97·18
10 c.c. = 0·15886 ,, ,, ...	47·5 ,,	0·15673	97·06
10 c.c. = 0·09926 ,, ,, ...	29·4 ,,	0·96593	97·30
10 c.c. = 0·1154 ,, ,, ...	35·1 ,,	0·11532	99·90
Glycerins containing Chlorides.			
	Grm.	C.c.	
10 c.c. contained—Glycerin ..	0·0915 Volume of hypo. (total) ..	28·5	
KCl	0·00585 Volume nitrate of silver ..	0·8	
	Actual volume of glycerin ..	27·7	0·91005 98·47
10 c.c. contained—Glycerin ..	0·0877 Volume of hypo. (total) ..	27·9	
NaCl	0·0108 Volume nitrate of silver ..	1·8	
	Actual volume of glycerin ..	26·1	0·08574 97·90
Recovered Glycerin—			
10 c.c. contained—Glycerin ..	0·1766 Volume of hypo. (total) ..	27·3	
NaCl	(found) Volume nitrate of silver ..	3·7	
	Actual volume of glycerin ..	23·6	0·07753 43·91

The method we have adopted is more simple, and consists of titrating the glycerin directly, and subtracting from the volume of the hyposulphite used that accounted for by the chlorides. The principle of the estimation is therefore as follows:—

1. In a known volume of the solution of impure glycerin we estimate the chlorine by the volumetric method, and obtain thus a volume V of hyposulphite.

2. If we submit the mixture of glycerin and chloride to the action of iodic acid, not only is the glycerin burnt under the circumstances described above, but the chloride also is decomposed with the liberation of iodine according to the equation:—

$$I_2O_5 + 10HCl + 10KI = 10KCl + 5H_2O + 6I_2,$$

according to which 10 molecules of hydrochloric acid correspond to 12 atoms of iodine, or again 355 of chlorine to 1524 of iodine.

Now, 1 c.c. of decinormal iodine is equivalent to 0·0127 grm. of iodine.

Therefore, if x represents the volume of this solution containing 0·01524 grm. of iodine, we find that this volume is given by the equation:—

$$x = \frac{1 \times 0{\cdot}01524}{0{\cdot}0127} = 1{\cdot}2 \text{ c.c. of N/10 iodine.}$$

This gives the following proposition:—If V is the total volume of decinormal hyposulphite, and if v represents the volume of decinormal silver solution, used to estimate the chloride, to transform this latter into the actual value of hyposulphite it suffices to multiply v by the factor 1·2. By subtracting this product ($v \times 1{\cdot}2$) from V, the difference $V-(v \times 1{\cdot}2)$ will give the iodine corresponding to the glycerin only.

Example:—Let V = 28·6 c.c., the amount of decinormal hyposulphite found, and v = 0·8 c.c. the amount of decinormal nitrate of silver; then we have 28·6 c.c. $-(0{\cdot}8 \times 1{\cdot}2)$ = 27·64 c.c., and the weight of the glycerin will be found by the equation, $W = 27{\cdot}64 \times 0{\cdot}0127 \times 0{\cdot}2587$.

Details of the Operation.

We prepare a solution of impure glycerin of about 1 per cent strength.

1. On 50 c.c. of this solution we estimate the chlorides directly with decinormal silver solution, using neutral chromate of potassium as indicator and carbonate of lime to neutralise the acidity if it exists; the volume found thus is calculated for 10 c.c.; call this v.

2. Take 10 c.c. of the solution of glycerin and place it in the flask, add successively sulphuric acid, iodic acid, and a fragment of marble, and proceed with the distillation under the same conditions as already described; titrate with hyposulphite; let V be the volume obtained, we subtract the volume v, transformed, as has been said, into iodine, and the difference multiplied successively by the corresponding factors is transformed into glycerin; finally, the result is calculated per 100.

Recovered Glycerin.

Certain industries, such as soap making and the manufacture of some pharmaceutical products (glycerophosphate of lime), leave glycerins charged with chloride of sodium and sometimes other salts. These glycerins are concentrated, the salt which separates is removed, and the recovered glycerins used again in manufacture. Their analysis is effected in the same manner as we have described; only, in the case of the glycerophosphates, the solution contains phosphoric acid; the chlorine is estimated by Wohlard's method, and the operation is carried out as above.

We propose applying this method of estimation to the determination of the glycerin in certain liquors of fermentation, and also to some pharmaceutical preparations. —*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 12.

ON THE ACTION OF CARBONIC OXIDE ON FERROCYANIDE OF POTASSIUM IN SOLUTION.

By J. A. MULLER.

It is a known fact that carbonic oxide acting on ferrocyanide of potassium in solution gives carbonyl-ferrocyanide of potassium, and that the transformation of the ferrocyanide into the carbonyl-ferrocyanide may become total, or practically so, in the presence of a sufficient excess of carbonic oxide.

Now, carbonic oxide also gives carbonyl-ferrocyanide of potassium when acting on dissolved ferricyanide of potassium, and the transformation is not preceded by a preliminary formation of ferrocyanide, as we should be inclined to believe *a priori*, but it is formed directly, as will be seen later on.

I have made a number of experiments by heating solutions of ferricyanide of potassium in an atmosphere of carbonic oxide in sealed tubes at about 130°. When the carbonic oxide is in sufficient excess I have always obtained carbonyl-ferrocyanide as the principal product of the reaction, and, in much less quantity, ferrocyanide of potassium; further, there was a production of formate and bicarbonate of ammonia as well as free carbonic

anhydride. Finally, the liquid in the tubes held in suspension a very slight greenish precipitate containing iron, and also a little potassium. This precipitate is soluble in fuming hydrochloric acid, giving a yellow colouration; when treated with water the solution changes from yellow to prussian-blue. I have taken for the composition of this precipitate—of which the weight never exceeded a few hundredths of the ferricyanide used—the formula $KFe_2\overline{CN}_6$, which represents ferrocyanide of potassium in which 3 atoms of this metal would be replaced by 1 atom of ferric iron. The amount of the precipitate in question was proportionally less as the transformation of the ferricyanide into carbonyl-ferrocyanide was more complete.

From an examination of the estimations made, the action of carbonic oxide on ferricyanide of potassium in solution may be expressed by the two simultaneous and independent reactions which follow, when the gas is in excess:—

$$a.\ 6K_3Fe\overline{CN}_6+7CO+15H_2O=$$
$$=6K_3FeCO\overline{CN}_5+4HCO_2NH_4+2HCO_3NH_4+CO_2.$$

$$b.\ 7K_3\overline{CN}_6+3CO+15H_2O=$$
$$=5K_4Fe\overline{CN}_6+KFe_2\overline{CN}_6+6HCO_2NH_4+3CO_2.$$

The two following experiments—in which nearly all the compounds formed were estimated, and in which the weights of these compounds were calculated according to the two preceding reactions—show an agreement between the numbers thus calculated and those given by analysis.

These experiments were carried out by heating for eighty hours, at 130—135°, aqueous solutions containing respectively 0·510 grm. of ferricyanide in 5 c.c. and 1·039 grm. of the same salt in 10 c.c. in the presence of an excess of carbonic oxide.

In the following table all the gaseous volumes are reduced to 0° and 760 m.m. in the dry state:—

	Expt. A.	Expt. B.
$K_3Fe\overline{CN}_6$ used	0·510 grm.	1·039 grm.
CO used	77·1 c.c.	79·4 c.c.
CO absorbed—Found	30·6 ,,	47·4 ,,
Calculated	31·4 ,,	55·0 ,,
CO_2 formed—Found	6·7 ,,	14·9 ,,
Calculated	6·2 ,,	16·0 ,,
$K_3FeCO\overline{CN}_5$ formed (*a*)	0·467 grm.	0·818 grm.
$K_4Fe\overline{CN}_6$ formed (*b*)	0·025 ,,	0·189 ,,
a+*b* corres. to $K_3Fe\overline{CN}_6$	0·496 ,,	1·050 ,,
HCO_2NH_4 formed—Found	—	0·125 ,,
Calculated	—	0·136 ,,
HCO_3NH_4 formed—Found	0·039 ,,	0·061 ,,
Calculated	0·037 ,,	0·065 ,,

It results from the figures in the above table that the centesimal compositions of the ferrocyanides formed under these conditions are as follows:—

	A.	B.
$K_3FeCO\overline{CN}_5$	94·9	81·2
$K_4Fe\overline{CN}_6$	5·1	18·8
	100·0	100·0

As can be seen, in the presence of a large excess of carbonic oxide, the reaction *a* takes place almost exclusively, and the reaction *b*, that is to say, the one that gives rise to the formation of ferrocyanide, has an entirely secondary importance.

This experiment shows plainly that the transformation of the ferricyanide into carbonyl-ferrocyanide is direct; for if ferrocyanide was formed first according to reaction *b*, and the carbonyl-ferrocyanide according to the well-known reaction—

$$K_4Fe\overline{CN}_6+CO+2H_2O=K_3FeCO\overline{CN}_5+HCO_2K+NH,$$

the amount of CO_2 formed would be much greater than that observed. Further, 7 molecules of ferricyanide would only thus furnish 5 molecules of carbonyl-ferrocyanide, while in experiment A 1 molecule of ferricyanide was transformed almost integrally into 1 molecule of carbonyl ferrocyanide.

Finally, in this latter experiment the greenish precipitate, to which I gave provisionally the composition $KF_2\overline{CN}_6$, was entirely negligible, so that if the ferricyanide had commenced by forming ferrocyanide according to equation *b*, this precipitate should have been, on the contrary, very considerable.*

In my experiments on the action of carbonic oxide on ferrocyanide of potassium, I have found that no reaction takes place in the absence of water (*Bull. Soc. Chim.*, vol. xxi., p. 475); the same is the case with ferricyanide of potassium, whice does not react with carbonic oxide in the dry state.—*Bull. Soc. Chim.*, Series 3, vol. xxix., p. 24.

RICKARDITE: A NEW MINERAL.

By W. E. FORD.

The new mineral to be described in this paper was first brought to the writer's attention by Mr. T. A. Rickard, of New York. A qualitative examination proved that in contained copper and tellurium, and no such combination having been hitherto described, the mineral seemed worthy of investigation. Through the courtesy of Mr. Rickard, sufficient material was afterward obtained for making a quantitative analysis, the results of which are given below.

Rickardite occurs at Vulcan, Col., in the Good Hope mine, owned by Dr. Loui Weiss. The vein mineral is chiefly pyrite, with which occurs native tellurium in unusually large masses, some of which measure fully three inches across. Other associated minerals are petzite, beithierite in imbedded prisms resembling stibnite, and a greenish-brown micaceous substance, perhaps roscoelite. A large body of native sulphur also was found in the vein. Rickardite itself occurs in small lense-shaped masses, generally rather intimately associated with native tellurium.

The material for analysis was broken up and carefully gone over by hand to free it from any adhering gangue, and only perfectly clean and homogeneous fragments were used. The method of analysis was simple. The powdered mineral was oxidised by nitric acid, which was subsequently removed by evaporation with sulphuric acid. To the strong sulphuric acid solution a liberal amount of hydrochloric acid was added, and then sulphur dioxide gas was led into the solution, which precipitated the tellurium in metallic form. This precipitate was filtered on to a Gooch crucible, dried in the air-bath at 100° C., and then weighed. In the filtrate copper was precipitated by hydrogen sulphide and determined as cuprous sulphide by igniting in a stream of hydrogen. Careful tests were made for gold, silver, lead, selenium, sulphur, arsenic, and antimony, with only negative results.

The analysis follows:—

	I.	II.	Average.	Atomic ratios.
Cu =	40·68	40·81	40·74	0·6469 = 4·00
Te =	59·36	59·06	59·21	0·4737 = 2·93
Total	100·04	99·87	99·95	

These results give the ratio Cu : Te = 4·00 : 2·93, or very nearly 4·00 : 3·00, and the formula for Rickardite therefore is Cu_4Te_3. This gives as the theoretical composition of the mineral, Cu = 40·51; Te = 59·49, which agrees very closely with the analytical determinations. Rickardite is therefore not only a new mineral but also a new type of

* It should be remarked that the theoretically possible attack of the precipitate $KFe_2\overline{CN}_6$ by CO would give ferric carbooyl-ferrocyanide, $Fe_2COC\overline{N}_6$, in the form of a violet precipitate; this has never been observed,

telluride, for no such four to three relation between metal and tellurium has hitherto been noted in the group of tellurides. The mineral may be regarded as consisting of one molecule of cuprous telluride and two of cupric telluride, $Cu_2Te.2CuTe$.

Rickardite has an unusual and beautiful purple colour, which rivals in intensity the deepest purple tarnish ever seen on chalcopyrite or bornite. The colour, however, in the case of Rickardite is not due to any tarnish, for it shows on a fresh fracture, and the powder of the mineral, even when ground very fine, is of the same deep colour. The mineral is massive in character, with an irregular fracture. Its hardness is 3·5 and its specific gravity was determined as 7·54. It is fusible at 1 and gives a pale azure blue flame colour tinged in the outer parts with green. Alone on charcoal before the blowpipe it gives a white coating of TeO_2 and fuses to a brittle globule of copper telluride. Fused with sodium carbonate and borax on charcoal it gives a coating of TeO_2 and a brittle globule of telluride, yielding only with considerable difficulty a malleable globule of copper. Roasted in the open tube the mineral fuses to a semi-transparent mass of brown colour, which is apparently some combination of the oxides of tellurium and copper, and only a faint sublimate of TeO_2 is formed on the walls of the tube. Heated in the closed tube it fuses and undergoes no further change. Heated in concentrated sulphuric acid it gives the characteristic reddish-violet colour of tellurium. When dissolved in nitric acid, the solution neutralised with ammonium hydroxide gives the deep blue colour of copper.

It is a pleasure to name the mineral Rickardite, after Mr. T. A. Rickard, the editor of the *Engineering and Mining Journal* of New York, who obtained the material for investigation and supplied the data as to its occurrence. Thanks are also due Dr. Weiss, of the Good Hope mine, who has been careful to secure all specimens which might be of scientific interest. In conclusion, the writer wishes to express his indebtedness to Prof. S. L. Penfield for his constant advice and assistance during the preparation of this article.—*American Journal of Science*, [4], xv., No. 85.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1902.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, January 10th, 1903.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 204 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, taken daily, from December 1st to December 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 204 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The shortage of rain still continues, the actual rainfall measured at Oxford during the month is 1·33 inches, the average fall is 2·16 inches; this leaves a deficit of 0·83 inch, and when added to the previous one of 7·9 inches, makes a total deficit for the year of 8·73 inches, or 34·5 per cent on the thirty-five years' average. There has not been an excess of rain in the Thames valley since June, 1900, though in July, 1901, the deficit was reduced to 0·9 per cent; during 1902 the deficit has never been below 30·5 per cent. It will be observed in Table A that there has been a deficit of rain in every month throughout the year; this is the first time such a thing has been recorded since we began our monthly records of the rainfall in January, 1893, exactly ten years ago.

TABLE A.—*Rainfall in Inches at Oxford, Month by Month, during the Year* 1902.

	Actual fall.	Mean of 35 years.	Difference from the mean.	
	Inches.	Inches.	Inches.	
January ..	0·66	2·08	−1·42	—
February ..	0·95	1·80	−0·85	—
March ..	1·20	1·47	−0·27	—
April	1·21	1·61	−0·40	—
May	1·53	1·75	−0·22	—
June	1·96	2·10	−0·14	—
July	0·62	2·49	−1·87	—
August ..	2·20	2·38	−0·18	—
September .	1·11	2·39	−1·28	—
October ..	1·55	2·76	−1·21	—
November..	2·24	2·30	−0·06	—
December ..	1·33	2·16	−0·83	—
	16·56	25·29	−8·73	—

Our bacteriological examinations of 359 samples have given the results recorded in the following table; besides these we have examined 248 other samples, from special wells, standpipes, &c., making a total of 607 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	377
New River, filtered (mean of 70 samples) ..	25
Thames, unfiltered (mean of 25 samples) ..	5885
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 190 samples)..	39
Ditto ditto .. .. highest	358
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 25 samples) ..	326
River Lea, from the East London Company's clear-water wells (mean of 24 samples) ..	50

Of the 284 daily samples taken from the filter-wells of the Metropolitan Water Companies, and examined bacteriologically by us, five samples, or 1·7 per cent, were sterile; twenty-three samples, or 8·1 per cent, contained more than 100 microbes per c.c.; and fourteen of these samples contained more than 150 microbes per c.c. The mean number of microbes in the twenty-three samples containing more than 100 microbes (which we regard as a good standard of purity) was 177, against a corresponding mean of 165 in twenty-seven samples during November. The water supply in December, on the whole, has maintained an equal microbic purity to that of November. This exceptional condition of the supply for the winter months is no doubt due to the absence of floods in the Thames Valley, and to the unusually mild character of the season. If the large deficit in the rainfall is made up, no doubt there will be in the near future a period when the filtration of the London waters will require more than usual care. As the general filter-beds are, however, in good working order, we believe these difficulties, should they arise, will be overcome satisfactorily.

TABLE B.—*Table showing Average Monthly Bacterial Variations during the Year* 1902.

Month.	Thames, unfiltered.	Thames-derived Companies, filtered.	New River, unfiltered.	New River, filtered.	River Lea, unfiltered.	River Lea (East London), filtered.	
January	4396	30	231	15	233	7	
February	3329	27	197	9	233	8	
March..	2013	28	336	13	710	12	
April	10652	31	282	9	545	26	
May	2896	31	193	12	371	37	
June	4338	32	312	16	464	35	
	4604	29	258	12	426	21	Mean of 1st 6 months.
July	2172	14	292	7	250	44	
August	5134	21	304	13	233	33	
September	2491	28	166	14	205	20	
October	8243	20	314	11	243	17	
November	2262	35	277	16	253	13	
December	5885	39	377	25	326	50	
	4364	26	288	14	251	29	Mean of 2nd 6 months.
	4484	27	273	13	338	25	Mean of 12 months.

TABLE C.—*Average Number of Microbes in the Filtered London Waters for the Past Six Years.*

	Thames-derived Companies.	New River.	River Lea.
1897	46	32	62
1898	34	30	25
1899	27	15	20
1900	21	9	10
1901	24	10	22
1902	27	13	25

TABLE D.—1902.—*Averages of the Supplies derived from the River Thames.*

	Common salt per gallon. Means.	Nitric acid per gallon. Means.	Hardness. Degrees. Means.	Oxygen required per gallon. Means.	Organic carbon per gallon. Means.	Organic carbon per gallon. Maxima.	Colour. Brown : Blue. Means.
January	2·448	1·134	15·59	0·059	0·152	0·197	21·0 : 20
February	2·299	1·078	16·47	0·041	0·119	0·160	12·7 : 20
March	2·368	0·903	15·71	0·058	0·151	0·208	17·4 : 20
April	2·345	0·840	14·97	0·047	0·136	0·164	14·9 : 20
May	2·248	0·700	13·94	0·042	0·118	0·150	13·2 : 20
June	2·266	0·727	13 61	0·051	0·128	0·142	13·8 : 20
July	2·339	0·611	13·52	0·055	0·131	0·213	17·1 : 20
August	2·171	0·652	12·78	0·041	0·098	0·132	11·1 : 20
September	2·347	0·760	12·77	0·039	0·099	0·129	13·8 : 20
October	2·347	1·009	13·45	0·038	0·093	0·116	11·3 : 20
November	2·334	0·873	14·13	0·039	0·105	0 129	12·3 : 20
December	2·329	0·971	14·44	0·059	0·166	0·224	22·6 : 20

The standard of general organic purity during the past year, as defined by chemical methods, has been maintained. As regards the month of December, the Thames-derived Companies show decided differences among themselves, which, as the supply comes from the same source, are essentially connected with differences in storage capacity and variations in the structure of the filter-beds, although the latter is of less importance in removing soluble organic matter.

The longer our experience of the bacteriological method, as applied to the analysis of the filtered supply, and the wider its application, the more we are convinced of its primary importance as a safeguard to the public. It enables us to define in a much more delicate way than is possible by chemical analysis what is an efficiently filtered water, and thereby enables the chemist to warn the engineer the moment any one of his filters shows signs of defective working. Whether the supply as regards the organic matter in solution varies more or less according to the season of the year, is of relatively small moment as compared with the knowledge that the microbic impurity is reduced to a minimum.

During the past year we have examined 6953 samples of London waters bacteriologically, as compared with 6893, 6731, and 4792 respectively in the three previous years. We have also made 2570 chemical analyses of London waters throughout this period, making a total of 9523 samples examined during the year.

The results of the filtration of the London waters are given in Tables B, C, and D.

Table B shows that during the first six months the Thames-derived Companies' clear-water wells contained on an average 29 bacteria per c.c., while the New River and River Lea supplies contained respectively 12 and 21. During the second six months, the number of bacteria in the waters from the three sources were respectively 26, 14, and 29.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

Cellular Structure of Amorphous Bodies.—G. Cartaud.—The free surface of certain fusible metals when rapidly solidified presents the aspect of microscopic cellular tissue. An unexpected phenomenon noticed on the surface of zinc amongst other metals is the constant presence in each cell of a circular centre in relief. The author investigates the surfaces of both crystalline and non-crystalline bodies, such as collodion, aluminium, glass, &c.—*Comptes Rendus*, cxxxvi., No. 1.

NOTICES OF BOOKS.

The New Volumes of the Encyclopædia Britannica. The Ninth of the New Volumes, being Vol. XXXIII. of the Complete Work. London: *The Times*. Edinburgh: Adam and Charles Black. 1902. Pp. 945.

This volume commences with STR (Strachey, Sir John) and completes the alphabet with ZWO (Zwolle).

The article on "The Sun," by Prof. Simon Newcomb, Ph.D., &c., will be read with interest not only by physicists but by the general reader. The writer gives in a few pages a concise summary of the accepted constitution of the sun as revealed by modern astronomical observations and by spectrum analysis, together with a few remarks on sun-spots, prominences, the corona, &c.

The subject of "Telegraphy" is divided into four headings, viz., theory, land telegraphy, submarine telegraphy, and wireless telegraphy. At the present time wireless telegraphy is attracting universal attention, chiefly owing to Marconi's remarkable achievement in signalling across the Atlantic by this means. The idea of sending electrical signals without the aid of a metallic circuit or wire is by no means new. In 1842 Morse showed that it was possible to interrupt the metallic circuit in two places and yet retain power of electric communication; his plan was to place four metallic plates opposite each other in pairs, at a wide distance apart in a canal, a battery and key being in circuit on one side and a galvanometer on the other; it was found to be easy to send signals by this method. It was the discovery by Hertz in 1887 that the discharge of a condenser produced an electric wave that brought about the possibility of wireless telegraphy as we now know it. Since then there have been several distinguished men at work on the subject, among the best known being Sir Oliver Lodge; he was followed by Marconi, who has worked indefatigably to bring wireless telegraphy to a practical success.

The "Telescope" is dealt with by Prof. S. Newcomb, and the "Telephone" by Prof. C. R. Cross.

"Thermochemistry," by Prof. James Walker, and "Thermodynamics," by Prof. H. L. Callendar, are both important subjects, and are treated at considerable length. From the standpoint of the conservation of energy the relation between chemical and thermochemical action bears the following aspect:—"A given amount of any substance under given conditions possesses a perfectly definite amount of intrinsic energy, and no matter what chemical and physical transformations the substance may undergo, it will, when it returns to its original state, possess the original amount of intrinsic energy." Since the intrinsic energies of different systems are invariable, the difference is constant, so that the heat evolved when one is changed into another is equal to the heat absorbed when it is converted back again.

Amongst metallurgical subjects "Tin" is briefly mentioned in a short article by Prof. H. Louis, and "Zinc" by Mr. F. L. Clerc.

There is an appreciative biographical notice of the late Prof. Tyndall, by Sir Oliver Lodge. In the limited space available it is not possible to enter very fully into the life and work of this distinguished chemist. His life has been roughly divided into four periods:—(1) The youthful period, dominated by study in Germany and work in magnetism; (2) the slatey cleavage and Swiss glacier period; (3) the Royal Institution, and radiant heat period; and (4) the final period, including his work on light houses, dust and disease, and "amateur theology." One important practical result of Tyndall's demolition of the "spontaneous generation" fallacy is the method of intermittent sterilisation at a moderate heat, sufficient to kill the developed micro-organisms, instead of by one fierce heating, attempting to attack the more refractory undeveloped spores of the same.

"Water Supply," by Mr. G. F. Deacon, forms an interesting article which should not be overlooked. He deals with the subject in a thorough manner, starting with collecting grounds, rainfall, evaporation and absorption, &c., all of which have to be carefully considered by the water engineer. Several pages are devoted to dams, and two excellent photogravures are given, showing the dam at Lake Vyrnwy, which supplies Liverpool with water. The first picture was taken in June, 1888, and shows the valley as it was; the second picture, taken in December, 1889, from the same position, shows the valley full of water. Continuing, we find a section on the purification of water, in which the construction and action of sand-filters in removing microbes is described; sedimentation is a great help to filtration, and with the two combined there should be no difficulty in reducing the number of bacteria in waters by 99 or 99·5 per cent.

Among other articles of scientific as well as general interest we may mention "Electric Welding" by Prof. Elihu Thomson; "Surgery," by Edmund Owen, F.R.C.S.; "Technical Education," by Sir Philip Magnus, &c.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 1, January 5, 1903.

Composition of the Gases issuing from Mont Pelée. Orgin of Volcanic Phenomena.—Armand Gautier.—An analysis of the gases issuing from Mont Pelée shows that they are identical with the gases obtained by heating crystalline rocks of primitive earths to a high temperature in a vacuum. From this fact and the actual gases found the author attempts to explain in a scientific manner the origin of volcanoes.

Proportion of Hydrogen in the Atmosphere.—Armand Gautier.—The author once more investigates M. Leduc's objections to his conclusions as to the proportion of hydrogen in the atmosphere.

Activity of certain Salts of the Rare Earths as Oxidisers.—André Job.—The spontaneous oxidation of potassium-cerium carbonate, and the oxidations resulting from contact with it, is so marked that the author further examines this type of phenomena. Other salts of cerium exhibit the same reactions, and it is found that for atomic equivalent quantities cerium acetate has an activity at least as great as manganese acetate itself. Cerium acetate is a very stable salt, its solution when exposed to the air remains limpid and colourless, and shows no sign of spontaneous oxidation. In the course of his experiments the author finds a quite unexpected example of similar activity in the case of lanthanum, and a result of his experiments is that undoubtedly there exists a peroxide of lanthanum, a hitherto undiscovered fact. At present it is not certain whether or not this oxide corresponds to the hydrate precipitated by hydrogen peroxide. He is continuing his investigations on this matter.

Two New Methods of Synthesising the Oxyphosphinic Acids.—C. Marie.—The author gives details of two methods of synthesising oxyphosphinic acid, but the one which gives the best results rapidly and with quantitative exactness is the method in which hypophosphorous acid is used. The phosphorous acid in the same way as the phosphorous trichloride employed by Fossek only acts very slowly and always tends to give resins, especially in the presence of fatty aldehydes.

Bromo-isopyromucic Acid.—G. Chavanne.—The author's present researches, as well as those previously made, still do not enable him to definitely fix the composition of isopyromucic acid, but they seem to suggest the idea that it belongs to the group of those curious deriva-

tives of acetylacetic ether discovered by Demarçay, and whose composition has been the object of Wolf's recent researches. It would then have a formula of the form $R<\frac{C(OH)=CH-CO}{R'\text{————}O}$, and would possess a lactonic group juxtaposed to an enolic group.

Oxidation of Ammonia and the Amines by Catalytic Action.—A. Trillat.—Catalytic action takes place with great activity on ammonia, in presence of water, the ammonia being transformed into nitrite and nitrate; the amines of the fatty series are decomposed, giving products of oxidation resulting from the catalytic action on the ammonia and the alcohols; finally, in the case of the aromatic amines, the oxidation seems to take place chiefly on the chains containing alkyl groups.

MISCELLANEOUS.

Proposed Society of Electro-Chemists and Metallurgists.—We have much pleasure in drawing attention to the subjoined circular-letter, which has been sent to a large number of electricians, chemists, and other scientific men:—

82, Victoria Street, London, S.W.,
January, 1903.

DEAR SIR,—At a meeting of the Provisional Committee of the proposed Society of Electro-Chemists held on January 6th, at 82, Victoria Street, S.W., Mr. James Swinburne in the chair, it was resolved, in consideration of the support and encouragement received in response to the circulars recently issued, to hold a General Meeting of the supporters of the movement, and formally inaugurate the work of the Society and elect a President and Council. The meeting will be held, by kind permission, at the rooms of the Faraday Club, St. Ermin's Hotel, Westminster, on Wednesday, February 4th, at 5 p.m., and the pleasure of your attendance and co-operation is cordially invited. Should you be unable to be present at the meeting I shall be glad if you will kindly send me your name as an intending member of the Society, if you have not already done so. It has been suggested that there should be two classes of Members—Members and Associated Members—the subscription fees being Two Guineas and One Guinea respectively.—Yours faithfully, F. S. SPIERS, Hon. Sec. of Provisional Committee.

The following Gentlemen have kindly consented to be nominated as Members of Council of the proposed Society at the Meeting to be held on February 4th:—*President*—J. W. Swan, F.R.S. *Vice-Presidents*—Prof. A. Crum-Brown, M.D., D.Sc., F.R.S.; Sir Oliver T. Lodge, D.Sc., F.R.S.; Ludwig Mond, Ph.D., F.R.S.; Lord Rayleigh, D.C.L., F.R.S.; Alexander Siemens, M.Inst.C.E.; J. Swinburne, Pres. I.E.E., M.Inst.C.E. *Council*—George Beilby; Bertram Blount; W. R. Cooper, M.A., B.Sc.; Sherard Cowper-Coles; F. G. Donnan, M.A., Ph.D.; Prof. A. K. Huntington; F. Mollwo Perkin, Ph.D.; W. S. Squire, Ph.D.; O. J. Steinhart, Ph.D.

Royal Institution.—On Thursday next, February 5th, at 5 o'clock, Sir Clements Markham will deliver the first of a course of three lectures at the Royal Institution on "Arctic and Antarctic Exploration," and on Saturday, at 3 o'clock, Mr. A. B. Walkley begins a course of three lectures on "Dramatic Criticism." Mr. G. R. M. Murray being unable owing to illness to deliver his course of lectures beginning Thursday, February 26th, Professor L. C. Miall will instead deliver three lectures on "Insect Contrivances." The Friday Evening Discourse on February 6th will be delivered by the Right Hon. Sir Herbert Maxwell, on "George Romney and His Works"; on February 13th by Professor S. Delepine, on "Health Dangers in Food": and on February 20th by Principal E. H. Griffiths, on "The Measurement of Energy."

MEETINGS FOR THE WEEK.

MONDAY, Feb. 2nd.—Society of Chemical Industry, 8. "Statistics of British and German Chemical Trades for 1901, with Suggestions for Improving the Official Tables," by F. Evershed. "The Standardisation of Analytical Methods," by H. Droop Richmond.
—— Royal Institution, 5. General Monthly Meeting.
—— Society of Arts, 8. (Cantor Lectures). "Paper Manufacture," by Julius Hübner.

TUESDAY, 3rd.—Royal Institution, 5. "The Physiology of Digestion," by Prof. Allan Macfadyen, M.D.
—— Society of Arts, 4.30. "Technical Education in connection with the Book-producing Trades," by Douglas Cockerell.

WEDNESDAY, 4th.—Society of Arts. 8. "Methods of Mosaic Construction," by W. L. H. Hamilton.

THURSDAY, 5th.—Royal Institution, 5. "Arctic and Antarctic Exploration," by Sir Clements Markham, K.C.B., F.R.S.
—— Chemical, 8. "A New Vapour-density Apparatus" and "A new principle for the Construction of a Pyrometer, by J. S. Lumsden.

FRIDAY, 6th.—Royal Institution, 9. "George Romney and His Works," by the Right Hon. Sir Herbert Maxwell, Bart., M.P., LL.D., F.R.S.

SATURDAY, 7th.—Royal Institution, 3. "Dramatic Criticism," by Arthur B. Walkley.

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THE CHEMICAL NEWS.

Vol. LXXXVII., No. 2254.

REVISION OF THE ATOMIC WEIGHT OF LANTHANUM.*

By BOHUSLAV BRAUNER, Ph.D.,
and
FRANTIŠEK PAVLÍČEK, Bohemian University, Prague.

(Continued from p. 52).

First Series of Determinations.

Table II. contains the results of the preliminary series of syntheses of lanthanum sulphate. The oxide, as well as the sulphate, was weighed after standing for half-an-hour over phosphoric oxide. The weights were carefully corrected, the method of weighing was that by vibrations, the weights are given *in air*. The standards used are O=16 and S=32·06.

In passing in review the atomic numbers obtained from the different fractions of lanthanum, they are seen to rise slowly from 138·78, corresponding with the most basic fraction La 1, to 139·08, corresponding with the least basic fraction La 7, after which follows the less pure fraction A 5+6, with a still higher atomic number 139·27. From this we might be entitled to conclude that the purest lanthanum material, which we have decomposed into eight different fractions, is not homogeneous. The difference between the highest and lowest number, 139·08−138·78=0·3, is not very considerable, but it must be said here that after resuming the work with increased refinements, two new sources of error were discovered which were removed by using a special arrangement for weighing.

New Fractionation.

In order to answer the question as to the homogeneity of our lanthanum, new methods were used for its fractionation:—

A. The purest lanthanum-ammonium nitrate was purified by a series of re-crystallisations and the atomic number was determined.

Experiment 15.—0·8262 grm. La_2O_3 yielded 1·4353 grm. of the "neutral" sulphate, SO_3=0·6091 grm., La_2O_3=57·563 per cent, whence La=138·89. This number corresponds to the mean of the above series.

B. The second method of fractionation consisted in digesting lanthanum oxide with a concentrated solution of ammonium nitrate at about 80°. The more basic portion of lanthanum may be expected to pass into solution, and the less basic portion to remain undissolved. We made use of the circumstance that the limit of this reversible reaction (which follows the law of mass action) is displaced in one direction as the temperature rises, whereas it is displaced in the contrary direction as the temperature falls. After repeating this process with the soluble portion (the reaction is reversed when ammonia is added) and with the insoluble portion very many times, the most basic fraction La α, and the least basic fraction La β were obtained. After purification from silica, &c., in the manner indicated (see p. 51), the hydroxide, oxalate, and oxide were prepared in turn, and the oxide was used for the atomic weight determination (weights *in air* are given). (See Table A).

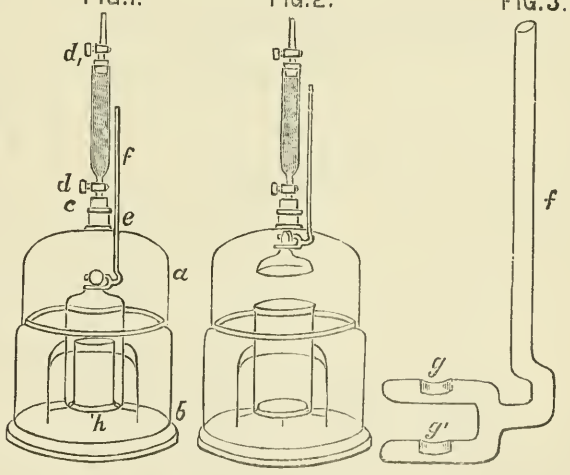
These results are opposed to those previously found. Lanthana separated from other cerite earths could not be split up into different fractions possessing a different atomic weight.

The above was the state of the experimental work when M. Pavlícek, in July, 1900, was obliged to leave the laboratory. With the intention of solving the question as to the real atomic weight of lanthanum with all possible accuracy, I undertook a further series of experiments which form a revision of the first part of this paper.

Second Series of Determinations.

It had now become obvious that the "sulphate method" of determining atomic weights is full of hidden small sources of error which were almost entirely overlooked by the earlier workers in the large series of determinations quoted in Table I., and were discovered and avoided only in this work only by degrees and not without difficulty and the sacrifice of much time. It must be remarked that the chemical method used in this part of the work was essentially the same as that described in the former part of this paper. The essential difference consisted in the manner in which the errors due to the hygroscopic nature of the material were avoided.

FIG.1. FIG.2. FIG.3.



The anhydrous sulphates of the rare earths are so extremely hygroscopic that it is impossible to weigh them in a *really anhydrous* state by using ordinary desiccators containing phosphoric oxide (Nilson) or to weigh them in closed weighing vessels made of light glass (Bunsen), as was done in the first part of this work. It was necessary to avoid the absorption of any trace of moisture during the process of cooling and weighing, and this was achieved by enclosing the crucible containing the still hot sulphate in a vessel containing completely dry air so that it could not come into contact with moist air until the weighing was finished.

I succeeded in doing this by constructing a desiccator shown in the Figures 1, 2, and 3.

* From the *Transactions of the Chemical Society*, 1902, vol. lxxxi.

Table A.

No. of experiment.	No. of fraction.	La_2O_3. Grms.	Sulphate "crude." Grms.	Correction. Grm.	SO_3 corrected. Grm.	La_2O_3 in the sulphate. Per cent.	Atomic weight La.
16.	La α	0·95652	1·66231	−0·00098	0·70481	57·576	138·98
17.	Most positive	0·45780	0·79580	−0·00015	0·33785	57·538	138·73
18.	La β	1·34754	2·34635	−0·00561	0·99320	57·569	138·93
19.	Most negative	1·17280	2·03961	−0·00157	0·86524	57·545	138·79

TABLE II.—*Syntheses of Lanthanum Sulphate. First Series (Preliminary).*

No. of experiment.	No. of fraction.	La_2O_3 (in air).	Sulphate "crude."	Correction.	SO_3 Corrected.	La_2O_3 in the sulphate.	Atomic weight La.
		Grms.	Grms.	Grm.	Grm.	Per cent.	
2.	La 1	0·93205	1·6198	Nil	0·68775	57 541	138·75
3.	La 1	0·8416	1·46366	−0 00132	0·62074	57·552	138·82
4.	La 1	0·85993	1·49518	−0·00078	0·63447	57·543	138·77
5.	La 2	0 7847	1·3635	Nil	0·5788	57·550	138·81
6.	La 2	0·80645	1·40145	Nil	0·5950	57·544	138·77
7.	La 3	1·0760	1·8707	−0·00157	0·79313	57·567	138·92
8.	La 4	1·0683	1·51479	Nil	0·7873	57·572	138·96
9.	La 5	0·8721	1·5160	−0·00151	0·64239	57·584	139·03
10.	La 6	0·9755	1·6948	−0·00099	0·71831	57·592	139·09
11.	La 6	0·9188	1·5955	Nil	0·6767	57·587	139·05
12.	La 7	0·9507	1·65212	−0 00172	0·6997	57·604	139·17
13.	La 7	0 9677	1·68194	−0·00132	0·71292	57·580	139·01
14.	A 5+6	0·8570	1·4880	−0·00064	0·63036	57·619	139·27

TABLE III.—*Syntheses of Lanthanum Sulphate. Second Series (Weights in Air).*

No. of experiment.	No. of fraction.	La_2O_3.	Sulphate crude.	SO_3 crude.	Correction.	SO_3 corrected.	Temperature.	La_2O_3.	Atomic weight of La. Apparent.	Atomic weight of La. True.
		Grms.	Grms.	Grms.	Grms.	Grms.		Per cent.		
20.	La 1	1·12533	1·95834	0·83301	—	—	510° One day.	—	138·23	—
			1·95809	0·83276	—	—	560° Two hours.	—	138·28	—
			1·95733	0·83200	—	—	560° Seven hours.	—	138·43	—
			—	0·83200	−0·00341	0·82859	—	57·5934	—	139·097
21.	La 1	1·70246	2·96305	1·26059	—	—	500° Seven hours.	—	138·17	—
			2·96227	1·25981	—	—	560° Six hours.	—	138·29	—
			—	1·25981	−0·00619	1·25362	—	57·5919	—	139·087
22.	La 1	1·02441	1·82295	0·79862	—	—	300° One day.	—	130·0	—
			1·78178	0·75737	—	—	500° Five hours.	—	138·42	—
			1·78168	0·75727	—	—	550° Eight hours.	—	138·44	—
			1·78001	0·75560	—	—	600—634° Six hours.	—	138·80	—
			1·77884	0·75443	Nil	0·75443	634—654° Seven hours.	57·5886	—	139·065
23.	La 0	1·06543	1·85312	0·78769	—	—	600–634° Half day.	—	138·43	—
			1·85125	0·78572	—	—	634—654° Two and a-half days.	—	138·82	—
			—	0·78572	−0·00133	0·78449	—	57·5933	—	139·097
24.	La 0	1·00676	1·74803	0·74127	—	—	634°± One day.	—	139·10	—
			1·74742	0·74066	—	—	654°± One day.	—	139·24	—
			—	0·74066	+0·00056	0·74122	—	57·5956	—	139·112
25.	La 7	1·06469	1·84850	0·78381	—	—	634°± One day.	—	139·125	—
			1·84820	0·78351	—	—	654°± One day.	—	139·19	—
			—	0·78351	+0·00028	0·78379	—	57·5980	—	139·128
26.	La 4	1·28627	2·23795	0·95168	—	—	634—654° Two days.	—	138·31	—
			2·23419	0·94792	—	—	> 654°± One day.	—	138·96	—
			—	0·94792	+0·00074	0 94718	—	57·5912	—	139·082
							Mean in air	57·5931		La = 139·095
							Probable error of the percentage ..	±0·00076		

On the bottom of the desiccator (*b*, Fig. 1), a thick layer of phosphoric oxide is placed, and in it stands a tripod made of thick copper wire. Into this tripod is placed loosely a light weighing glass provided with a perfectly ground *conical* stopper. The cover of the desiccator (*a*) has in its centre a neck closed by a perforated rubber stopper (*c*) carrying a small drying-tube filled with anhydrous calcium chloride and provided with two stopcocks (*d*) and (d_1). At a distance halfway between the centre and the edge of the upper part of the cover (*a*), a round hole of about 8 m.m. diameter is bored, and in this is fastened by means of rubber-solution a piece of thick-walled rubber tube (*e*) through which a glass fork (*f*) may be pushed and moved in both directions in a layer of "unguentum simplex." This fork serves to open, raise, and close the stopper of the weighing glass while the desiccator remains closed. The fork (Fig. 3) possesses two horizontal transverse furrows (*g* g_1) into which the handle of the glass stopper exactly fits. By pushing the fork downwards so that its teeth pass the handle of the stopper, and then turning the cover of the desiccator through 90°, the handle of the stopper falls into the furrows and rests upon them. The stopper is then easily raised and its point pressed against the rubber stopper (*c*); it rests firmly, so that the cover of the desiccator containing it may be taken off and even inclined without the stopper falling out. On the bottom of the weighing glass is placed a round table made of platinum sheet and provided with three legs.

When the platinum crucible with the hygroscopic substance (for example, La_2O_3) has been heated to a yellow heat, the desiccator is prepared as seen in Fig. 2, the lid taken off, and the still red-hot crucible placed on the platinum table (*h*) in the weighing glass, which prevents the glass from coming into direct contact with the red-hot crucible. The cover (*a*), which was taken off only for a few seconds, is replaced, the expanding hot air leaves the desiccator through the drying-tube (*d* d_1), and, on cooling, dry air passes in through the same way, so that the atmosphere of the desiccator is in equilibrium with the outer atmosphere. Then the stopper is pushed into the weighing glass so as to *almost* close it, which is done completely after a quarter of an hour, when all has cooled down. After this, the cover of the desiccator is turned back through 90°. The substance enclosed inside the weighing glass cannot attract moisture from anywhere. The surface of the phosphoric oxide inside the desiccator must be renewed very often and fresh oxide added.

The crucible was weighed regularly half-an-hour after being placed in the desiccator, and a weighing glass of the same size as that just described containing a similar platinum crucible treated in the same way was used as a tare on the right-hand pan of the balance, both weighing flasks having nearly the same weight and displacing nearly the same volume of air, so that their coefficient of surface condensation was equal in both cases.

The weighings were made on a very fine and sensitive balance made by Rueprecht, and reconstructed for this kind of work by Nemetz, of Vienna. The balance was guarded on all sides against the influence of radiant heat, and as fractions of a grm. could be placed on the balance without the case being opened, the change of the "zero-point" or of the "state of the balance" (Mendeléeff) was only very small. The "zero-point" was not taken with the empty balance, but with carefully adjusted 50 grm. weights on each pan, this being very nearly equal to the weight of the weighing glass *plus* crucible. The method of vibrations was used, and the weights employed were most carefully calibrated, so that the errors due to weighing alone hardly exceeded ± 0·00002 grm. This *physical* error is quite insignificant compared with the much greater error due to the inexactness of our *chemical* methods.

When by using the desiccator just described the attraction of moisture by the enormously hygroscopic lanthanum sulphate was reduced to a minimum, higher numbers were obtained for the atomic weight than in the first series. This is seen by comparing the results of experiments 17 and 19 obtained by M. Pavlicek by the old method of weighing, giving La = 138·73 and 138·79, with experiments 16 and 18 made by me, which yielded La = 138·98 and 138·93.

The results of this second series of syntheses are seen in Table III., and they require some explanation.

In order to be able to compare the data obtained in the different phases of the single experiments with those obtained by other chemists, the weight obtained by weighing *in air* are given in Table III., from which the "apparent" and "true" atomic weights are calculated.

For the final determinations of the atomic weight of lanthanum, the reduction to a *vacuum* was calculated by using the following data:—Density of $La_2O_3 = 6·48$, that of air in our laboratory $d = 1·18$ (1 litre = 1·18 grms.), 1 grm. La_2O_3 displaces 0·182 m.grm. of air or 1 grm. in air weighs in a vacuum 1·000182 grms. Density of $La_2(SO_4)_3 = 3·545$, 1 grm. in air weighs in a vacuum 1·000333 grms. The *vacuum numbers* with all other corrections are given in Table IV.

TABLE IV.—*Final Determinations of the Atomic Weight of Lanthanum (Weights in Vacuo).*

No. of fraction.	No. of experiment.	La_2O_3 grms.	$La_2(SO_4)_3$ grms.	SO_3 grms.	La_2O_3 per cent.	Atomic weight La.
La 0	23	1·06562	1 85054	0·78492	57·5842	139 036
La 0	24	1·00694	1·74856	0·74162	57 5863	139·053
La 1	20	1·12553	1·95457	0·82904	57·5845	139 038
La 1	21	1·70276	2·95707	1 25431	57·5828	139·026
La 1	22	1·02460	1·77943	0 75483	57·5802	139·009
La 4	26	1·28650	2·23419	0 94769	57·5823	139 024
La 7	25	1·06488	1 84910	0 78422	57·5891	139·068
				Mean	57·5843	139·036
				Probable error	± 0 0007	

The atomic weight of lanthanum corrected to a vacuum is therefore La = 139·04.

In all experiments recorded in Table III., the temperature to which the sulphate was heated was stated as nearly as possible. It was found that even at 560°, and when the heating was carried out in an atmosphere of ammonium carbonate, the acid sulphate could not be destroyed completely, and the "apparent" atomic weight of about 138·4 was obtained; this is identical with that found by several investigators who overlooked the presence of the acid sulphate. If, however, a larger mass of the sulphate had to be heated, the inner part gave off this "half-combined" sulphuric acid less easily than when the mass of the sulphate was smaller, so that, for example, with 1·82 grms. of the sulphate the value 138·42 (experiment 22) was obtained, whereas with 2·96 grms. this had fallen to 138·29 (experiment 21).

The attempt was made to heat the lanthanum sulphate to such a high temperature that some *basic sulphate* might be formed, in order to see whether the same atomic weight would be obtained when the titration was done from the *basic side*, instead of from the acid side as hitherto. For this purpose the smaller crucible was heated inside a larger platinum crucible to a dark red heat. It was found that the sulphate assumes a visible dark red heat near the temperature at which pure potassium iodide melts, that is, 634° ± 3° (Carnelley), whereas a stronger red heat corresponded to the melting-point of silver sulphate, that is, to 654° ± 2°.

When this mode of heating was used, a "neutral sulphate" was obtained only in experiment 22, and basic sulphates were obtained only in experiments 24 and 25. On titration with N/20 sulphuric acid until all basic salt had dissolved and the neutral point was reached, the same result was obtained as when the free acid was titrated with N/30 sodium hydroxide. This agreement shows that the final residue of "half-combined" sul-

phuric acid is present in the form of the *acid sulphate* and not of that of the pyrosulphate.

It is also seen from the above experiments that normal lanthanum sulphate may be heated to a dark red heat without decomposing, for its slight decomposition begins only at about 650°±, and even near this temperature the decomposition of the *acid* sulphate is not complete.

From Table IV. it is seen that the largest deviations from the mean atomic weight are +0·03 and −0·03, and the probable error of the percentage of the oxide in the sulphate is ±0·0007, so that the lanthanum material employed may be considered *homogeneous*. With regard to the circumstance that the oxide obtained from fraction La 7 was slightly buff-coloured, as compared with the white oxide obtained from the most basic fractions La 0, La 1, La 2, La 3, and La 4, the possibility that the fraction La 7 contains a trace of an impurity which also *very slightly* raises its atomic weight, is not excluded, but even if this experiment 25 and the too low result of experiment 22 be omitted, the mean atomic weight La=139·04 would remain unchanged. On the contrary, the lower fractions may be regarded as containing the real *pure lanthanum*.

This question was tested with a more negative and less intensely purified fraction A5+6.

Experiment 27.—0·90238 grms. La_2O_3 gave, after heating the sulphate for two days at 634°±, crude sulphate=1·56694 grms. (apparent atomic weight =139·07). The sulphate was acid, and the correction −0·00056 grm., therefore SO_3=0·66400 grm. La_2O_3 in the sulphate =57·609 per cent, from which La=139·20 (in air).

This result agrees with that obtained in experiment 14 of the first series, and shows that the assumption of the presence of an earth with a higher atomic weight in the less basic fractions of our lanthanum material beginning even with La 7 is not wholly unfounded.

The present series of experiments, however, did not confirm the slight variation of the atomic weight obtained from the lower fractions in the first series of experiments. The lower numbers obtained in that series, especially with the fractions La 1 and La 2, and the circumstance that the discrepancies between the first and second series gradually diminish, was found only after a long time to be due to the following reasons:—

(1) The highly hygroscopic nature of the salt. The water vapour which was attracted by the salt from an atmosphere of ammonium carbonate is given off again by the salt only after being heated for many hours at above 600°. If we stop this heating too early, the weight of the sulphate will be found *greater*, and the atomic weight *smaller*, than the truth. The same error is caused if the anhydrous sulphate is left in an ordinary desiccator, especially if it does not contain fresh phosphoric oxide and if no precautions are taken to avoid the attraction of moisture during the weighing of the salt. These two sources of error were eliminated only during the second part of the research by using the special form of desiccator.

(2) The titration of the acid sulphate in the presence of ethyl-orange is not only an *acidimetric*, but also a *colorimetric* method, which requires a well-lighted laboratory and good practice. Both were wanting during the first stage of our work. The use of this method undoubtedly lowers the standard of exactness of our work, for whereas the *weight* of the sulphate can be determined to ±0·00002 grm., the acidimetric-colorimetric method hardly allows an exactness equivalent to ±0·00005 grm. of sulphuric acid to be reached.

It is an interesting psychological fact that with increasing practice the sum of the errors due to the above sources gradually diminished, so that the results obtained during the latter part of the first series are quite free from them. This is especially the case with experiments 9, 10, 11, 12, and 13, which give a mean atomic weight almost identical with that obtained in experiments 20—26, but they are not included in the final calculation, as they would raise the value of the probable error of the mean from ±0·00073 to ±0·0012, and lower the "weight" of our atomic number. But the direction in which the errors of the first series diminish may be regarded as a proof that our present number, La=139·04, lies near the truth.

(To be continued).

NOTE ON BOILER WATER CONTAINING SODIUM CARBONATE.

By ARTHUR E. LEIGHTON.

In recent years some attention has been drawn to waters containing sodium carbonate as a constituent, and Fisher (*Analyst*, 1901, p. 202) has pointed out how commonly such waters are yielded by deep wells in the London area.

Although this is the case, but little information is extant as to the behaviour of such waters when used for boiler purposes. Some little time ago a sample of water was received which was said to have corroded the plates and gun-metal fittings of the boiler in which it had been used. That corrosion of the boiler plates had occurred was probable by reason of the quantity of iron oxide suspended in the sample, whilst the gun-metal check valve was corroded to a depth of one-sixteenth of an inch. It might be mentioned here that the "gun-metal" used for this purpose contains zinc in addition to copper and tin. An analysis of the filtered water was made with the following result. For comparison the figures relating to the well water are given, both series being stated in N/10 c.c. per litre:—

		Well water. N/10 c.c. per litre.	Boiler water. N/10 c.c. per litre.
Combined acids	CO_2 ..	55	284
	Cl ..	40·5	524
	SO_3 ..	29·65, 125·15	399·6, 1207·6
Combined bases	CaO ..	8·70	traces
	MgO .	8·15	traces
	Na_2O	108·4, 125·25	1510, 1510·0

In the original water the combined acids and bases exactly neutralised one another, and assuming that the calcium and magnesium are present as carbonates, this water contained of sodium carbonate 14 grains per gallon. In the boiler water there was an excess of base over acid to the extent of 302·4 N/10 c.c. per litre. Actual titration with phenolphthalein and methyl orange shows caustic soda equal to 307 N/10 c.c. per litre, or a 0·12 per cent solution. This caustic soda solution has been produced by concentrating the original well water about thirteen times in a boiler working under a pressure of 120 lbs. The solution readily attacked aluminium foil in the cold. Paul (Society of Engineers, November 21, 1891) records a similar case where water originally containing sodium carbonate has, after one month's run in a boiler and becoming concentrated about fifty times, developed caustic soda. He found the solution contained 163·24 grains per gallon, or 0·23 per cent caustic soda. In this case severe corrosion of the boiler had taken place. It shows with what discrimination soda-ash should be used for water softening. No explanation has yet been given of the formation of caustic soda under these conditions, and it is not easy to persuade a manufacturer to allow experiments to be carried on, especially so when these experiments must only result in further corrosion of the boiler. The following results obtained after a short run where the water concentration reached about 2 may be of interest:—

		Well water. N/10 c.c. per litre.	Boiler water. N/10 c.c. per litre.
Combined acids	CO_2 ..	46	77
	Cl ..	38	72
	SO_3 ..	27·6, 111·6	52·1, 201·1
Combined bases	CaO ..	5·3	2·3
	MgO .	6·15	1·2
	Na_2O	100·2, 111·65	196·4, 199·9

No caustic soda had been formed. Judging from the state of the water after the last experiment, frequent blowing down of the boiler would have prevented the formation of caustic soda, but in the case under notice such treatment would have been highly inconvenient. Chemical treatment was resorted to—the "half bound" and free carbonic acid being removed by lime, and the sodium carbonate by calcium chloride.

CARBON IN HIGH-SPEED STEELS.

Amongst published methods for the estimation of carbon in steel and iron current forty years ago were some in which the carbon, after separating from the iron, was mixed with copper oxide and burned in a stream of oxygen with all the usual precautions common to the combustion of organic bodies. The use of copper oxide for this purpose has been abandoned long ago, along with many other time-absorbing or expensive modifications which were found to have no influence on the accuracy of the results obtained.

The simpler forms of the combustion process have gained the confidence of works' analysts even when applied to the assay of special steels; in fact, it is generally assumed that any steel (or alloy for that matter) which is decomposed by a solution of a double copper salt can have its carbon determined by igniting the residue and measuring the CO_2 formed.

There is evidence, however, that the high-speed self-hard steels, introduced three or four years ago and now commonly met with, are not amenable to the usual means of estimating carbon. The results are said to be low by 0·05 to 0·10 per cent when compared with those obtained by igniting the steel direct with red lead. This I can confirm, and even a greater deficiency might be attained with apparatus in all ways appropriate to the assay of normal steels.

These low results have so far been explained by the assumption that an acid solution of the double copper salt, as well as the hydrochloric acid used subsequently for washing, may decompose or dissolve a portion of the residual metallic carbides. This assumption is incorrect. It was found experimentally:—

1. That no hydrocarbons are evolved on dissolving these special steels in the usually acidified solution of copper ammonium chloride.
2. That the residual carbides contain all the carbon present in the steel weighed off; but the unusual amount of chromium and tungsten also in the residue prevents the carbon being entirely burned off except at a very high temperature, or after mixing with some oxidising reagent, such as copper oxide, lead chromate, or red-lead.

The demonstration of the second proposition alone is conclusive. It was made by assaying the steels in the usual manner, then grinding the ignited residue, mixing with red-lead, and re-igniting. The total weight of carbon dioxide obtained in these two ignitions agreed with that obtained from a direct combustion of the steel with red-lead, or with that obtained by mixing the residue at once with copper oxide as suggested in the first paragraph.

The carbonaceous residue obtained from these special steels is comparatively bulky, and is usually arranged in small compass in the boat, and frequently also under a layer of asbestos. A more nearly accurate result can be obtained by simple ignition if the residue is arranged more superficially in the boat. J. T.

Action of Methylic Alcohol on its Soda Derivative.—Marcel Guerbet.—Methylic alcohol heated with its soda derivative does not behave like the other alcohols; at 200° it remains unchanged; at 230—240° it decomposes with the production of sufficient gaseous products to cause the tube to explode.—*Bull. Soc. Chim.*, [3], xxvii., No. 12.

ARSENIC PENTACHLORIDE.*

By CHARLES BASKERVILLE and H. H. BENNETT.

The non-existence of arsenic pentachloride has for a long time been regarded as remarkable, especially so when the analogues of that element having atomic weights below and above it, phosphorus and antimony, show pentavalence toward the halogens.

Hurtzig and Geuther (*Ann. Chem. Pharm.*, cxi., 171) endeavoured to prepare it by treating arsenious acid with phosphorus pentachloride. Mayerhofer (*Ann. Chem. Pharm.*, clviii., 326) passed chlorine into arsenic trichloride at −10° C., removing the excess of chlorine by a stream of carbon dioxide, and failed to obtain the body. Janovsky (*Ber.*, 1875, viii., 1636) treated phosphorus pentachloride with arsenic trihydride at 0° C. with negative results. Dumas (*Liebig's Ann. Chem.*, xxxiii., 337) thought he had arsenic pentachloride, but Capitaine (*Journ. Pharm.*, xxv., 524) proved it to be a mixture of As_4O_6 and $AsCl_3$. Weber having prepared $SbCl_5PCl_5$, Cronander (*Ber.*, 1873, iii., 1466) sought its analogue $AsCl_5PCl_5$, but only obtained $AsCl_3PCl_5$. Marignac (*Liebig's Ann. Chem.*, cxlv., 249) obtained AsF_5 as a double fluoride of potassium. Sloane (Chemical News, 1881, xlvi., 194) prepared AsI_5, and endeavoured to secure the pentachloride by saturating arsenic trichloride with chlorine at −23° C. at ordinary pressure, and obtained the ratio As : Cl : : 1 : 4·447. There was a gradual decrease in the ratio up to 24° C., when it became 1 : 4·08, then there was an abrupt change rapidly approaching 1 : 3. Such observations made the existence of As_2Cl_8 quite conceivable.

Baeyer's pentahalogen compounds of arsenic, in which one to four chlorine atoms have been replaced by alkyl radicals, and Michaelis' (*Ber.*, viii., 1316; and ix., 1566) work with phenyl residues are well known. Recently the pentavalent organic arsenic compounds have become much augmented by the extensive work of Michaelis (*Liebig's Ann. Chem.*, 1902, cccxx., 271).

The procedure of Sloane (Chemical News, 1881, xlvi., 194) offered encouragement, provided the reaction should be carried out at a lower temperature. Chemically pure arsenic trichloride was prepared and re-distilled from concentrated sulphuric acid, and its purity determined by analysis. About 5 c.c. of the liquid were placed in a dry test-tube buried in solid carbon dioxide loosely packed in a Dewar bulb, and dry chlorine led in. The crystalline trichloride (m. p. −18° C.) assumed a greenish yellow colour and became liquid, which grew in bulk. Besson (*Comptes Rendus*, cix., 940) showed that arsenic trichloride saturated with chlorine at zero does not solidify at −30° C. Davy also showed that it does not freeze at −29° C. when well saturated with chlorine. After a few minutes, the time varying with different experiments, the stream of gas was cut off and the excess of liquid chlorine removed by fractional distillation. Chlorine boils at −33·6° C. We verified this by completely boiling away several c.c. of chlorine at −33° C. in other experiments. As a safeguard we allow the temperature to rise to −31° C. The liquid was cooled again to −35° C., and samples were removed as the temperature rose by means of a small pipette chilled to the temperature of the refrigerating agent. These samples in one experiment were placed directly in water; in another it was deemed better to place them in a dilute sodium hydroxide solution. In the former case immediate solution occurred with those portions removed at temperatures below −25° C., while at those higher a white precipitate, evidently of arsenious oxide, formed, increasing in amount with elevation of temperature. The orthoarsenic acid was determined as magnesium pyroarsenate and chlorine as silver chloride. The filtrate from the magnesium ammonium arsenate in the former was tested for the presence of arsenious compounds.

* Contribution from the Chemical Laboratory of the University of North Carolina. From the *Journal of the American Chemical Society*, vol. xxiv., No. 11.

None were found up to −25° C., when arsenious acid was found in traces increasing in amount with rise of temperature. The ratio between arsenic as arsenic acid, and chlorine, was 1 : 5 or $AsCl_5$. At −25° C. the ratio rose to 1 : 6. The loss of chlorine, and consequent return to the trivalent condition, became more and more marked, the higher the temperature.

The following analytical results were obtained for two temperatures in one experiment:—

Temperature. °C.	Amount taken.	Chlorine found. Per cent.	Theoretical.	Ratio obtained. As : Cl.
−35	0·1796	69·93	70·26	1 : 4·93
−25	0·26675	73·21	—	1 : 5·78

Arsenic pentachloride is readily soluble in carbon disulphide and absolute ether cooled to −30° C. From the latter, when chilled several degrees, it crystallises in yellow prisms. It loses chlorine when heated above −28° C, On exposure to the air it fumes, evolving hydrochloric acid vapour, and as the temperature rises forms crystals, most likely of the trichloride, which melt soon to the liquid state. A special preparation was made and sealed in a tube. The greenish yellow liquid when cooled to −38° or −40° C. (we had no thermometer for determining this accurately) formed beautiful yellow crystals.

It is not regarded necessary to give our several unsuccessful preliminary experiments to secure the body for analysis. Suffice it to say that placing the body in a pipette or weighing-bottle at the temperature of the air brought about its immediate decomposition to the original trichloride, chlorine being evolved.

AN OCCURRENCE OF FREE PHOSPHORUS IN THE SALINE TOWNSHIP METEORITE.

By OLIVER C. FARRINGTON.

On drilling into the Saline Township meteorite* recently for the purpose of breaking off a piece, a white "smoke" was observed by the writer to rise from the drill-hole when a depth of a little over two inches (5·5 c.m.) had been reached. This "smoke" had a pungent, garlic-like odour, which was recognised as similar to that of white phosphorus. It was more pungent and resembled the odour of burning arsenic to some extent, but on the whole suggested that of phosphorus more. It was at once surmised that phosphorus might exist in the free state in the meteorite, and the supposition was soon confirmed by the following tests:—

1. On shielding the eyes from the light and looking into the drill-hole, a luminous spot could plainly be seen at the bottom. This spot on further observation showed itself to be actually made up of two. One of these was fixed and central and the other moved around it, making a revolution every two or three seconds. This motion corresponded to the swirling movement with which the fumes rose from the hole, and doubtless represented the manner of supply of air to fresh portions of the phosphorus.

2. On holding a strip of paper saturated with silver nitrate in the fumes it turned black in a few moments.

3. On treating some of the powder from the drilling with nitric acid and adding the solution so obtained to ammonium molybdate, the familiar yellow precipitate of ammonium-phospho-molybdate was produced.

The fumes continued to rise from the hole for about two hours, when they gradually diminished in volume and disappeared. The odour could, however, be detected eighteen hours afterward. These observations were confirmed by several of my associates. No effort as has yet been made to obtain a quantitative determination of free phosphorus in the meteorite, nor is it likely that results of any particular value could thus be gained. Two holes were drilled the same depth as the first in other parts of the stone, but from neither was any repetition of the above-named phenomena observed. The phosphorus is (or was) probably, therefore, only locally distributed and in small quantity. The stone where broken at the end of the hole first drilled shows a spot about half-an-inch in diameter differing considerably in colour from the rest of the stone, being brownish-white in contrast to the greenish-black hue of the remainder. This portion may prove on further examination, therefore, to be differently constituted. The properties above described are those of free phosphorus, however, and the observations leave no doubt that it existed in the meteorite. This seems to be the first known instance, then, of finding this element existing in the free state in nature.

The occurrence serves to point several conclusions regarding the origin of meteorites, which, while they do not differ from those now generally held by students of these bodies, emphasise opinions which have at times been disputed. First, the meteorite was not formed upon the earth. Second, free oxygen was not present where it was formed. Third, the interior of the meteorite cannot have been subjected to any high degree of heat since its aggregation in the solid state.—*American Journal of Science*, [4], xv., No. 85.

* For a brief account of the fall and general characters of this meteorite see *Science*, N. S., vol. xvi., p. 67, July 11, 1902.

ON THE DETERMINATION OF LEAD IN ORES.*

By IRVING C. BULL.

(Concluded from p. 54).

Summary of Results.

The accompanying is a table of the results on the different ores as obtained by the various methods described; also a table of the interferences as they occur in each of these methods of analysis.

These results are percentages of lead.

First line = milligrms. of lead taken.

Second line = milligrms. of designated impurity taken.

Third line = milligrms. of lead found by use of designated method.

Fourth line = percentage of error (high = + or low = −) in terms of lead.

Conclusions.

After carefully reviewing the tables of results obtained on the ores and by weighted additions of impurities, it becomes evident by the nature of the closely agreeing results upon the ores that there are four volumetric methods for lead that should receive attention, namely, the molybdate or Alexander's, the dichromate or back titration with either a ferrous salt or by "hypo.," Koenig's, and the ferrocyanide.

By an examination of the interference table, we must at once conclude that the dichromate is more liable to be inaccurate than any of the others, unless a great deal of time is spent in washing out the foreign chromates which in many cases are sparingly soluble, therefore requiring a great deal of time.

Koenig's method is the one method where an inside indicator makes it advantageous; it is also fairly rapid to manipulate, and gives, with ordinary amounts of impurities, good results; however, in some ores erroneous results are quite apt to occur.

The methods which give very good results even in the presence of extraordinary amounts of impurities, are the

* Contribution from the Havemeyer Laboratories, Columbia University. From the *School of Mines Quarterly*, xxiii., No. 4.

Number of ores.	Fire assay.	Lead sulphate method.	Lead chromate method.	Electro-method.	Alexander's method.	Koenig's method.	Oxalate method.	Dichromate ferrous method.	Dichromate "hypo." method.	Ferrocyanide method.
I.	76	78·68	78·71	78·73	78·74	78·60	77·54	78·71	78·76	78·67
	—	78·62	78·68	—	78·82	78·64	77·60	78·78	78·73	78·65
II.	37	37·20	37·28	37·35	37·41	37·38	36·71	37·32	37·33	37·31
	—	37·26	37·30	—	37·44	37·40	36 62	37·38	37·37	37·29
III.	9	10·76	10·77	10·80	10·80	10·58	9·92	10·78	10·80	10·90
	—	10·74	10·74	—	10·83	10·62	9·98	10·72	10·76	10·86
IV.	24·7	18·40	18·45	18·58	18·47	18·46	17·54	18·48	18·50	18·44
	Base metal	18·43	18·40	—	18·51	18·42	17·65	18·44	18·45	18·48
V.	26·7	27·25	27·23	27·32	27·44	27·24	26·28	27·31	27·26	27·25
	—	27·21	27·20	—	27·35	27·26	—	27·27	27·32	27·18
VI.	37·8	38·50	38·47	38 60	38·66	38 60	37·38	38·46	38·57	38·65
	—	38·54	38·50	—	38·58	38·68	—	38·52	38 60	38·58

	Ferrocyanide.					*Dichromate Ferrous.*					*Koenig's.*					*Alexander's.*				
Antimony.	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300
	25	50	100	200	400	25	50	100	200	—	25	50	100	200	400	50	50	100	120	200
	300	300	300	300	300	313	342	351	405	—	300	300	300	300	300	300	300	300	300	300
	0	0	0	0	0	+4·1	+12·	+14·	+26·	—	0	0	0	0	0	0	0	0	0	0
Bismuth.	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300
	25	50	100	200	400	25	50	100	200	400	25	50	100	200	400	25	50	100	200	400
	300	301	304	305	306	310	323	349	421	563	300	300	300	300	300	300	300	300	300	300
	0	+0·3	+1·3	+1·6	+1·8	+2·	+7·	+13·	+28·	+46·	0	0	0	0	0	0	0	0	0	0
Barium.	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300
	12	25	50	100	200	12	25	50	100	200	12	25	50	100	200	12	25	50	100	200
	301	302	305	306	306	320	337	371	402	481	310	314	330	352	368	298	295	277	256	244
	+0·3	+0·6	+1·6	+1·8	+1·8	+6·6	+10·9	+19·	+25·	+38·	+3·2	+4·	+9·	+14·	+18·	−0·6	−1·6	−6·	−10·	−15·
Strontium.	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300
	25	50	100	200	400	25	50	100	200	400	25	50	100	200	400	25	50	100	250	200
	300	300	300	300	300	306	311	323	342	356	320	334	414	494	560	300	300	297	289	283
	0	0	0	0	0	+1·8	+3·5	+7·	+12·	+16·	+6·	+10·	+33·	+39·	+46·	0	0	−1·	−3·6	−5·9
Calcium.	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300
	25	50	100	200	400	25	50	100	200	400	25	50	100	200	400	25	50	100	150	200
	300	300	300	300	300	303	305	313	328	351	300	304	352	450	520	300	300	300	300	300
	0	0	0	0	0	+0·9	+1·6	+4·1	+8·2	+14·	0	+1·3	+14·	+33·	+42·	0	0	0	0	0

ferrocyanide and Alexander's methods. Both have the disadvantage of having outside indicators, where allowances must be made very carefully in order to get agreeing duplicates in analysis. The time required for the manipulation of either method is about the same, *i.e.*, about one hour, either requiring less time than any of the methods before discussed.

In concluding, therefore, the preceding work points out quite conclusively that the ferrocyanide titration method is at least one of the best methods for a lead assay in the wet way that is known at present, not only as regards rapidity, but also by its accuracy, having even a slight preference over Alexander's molybdate method in so far as interfering elements are concerned.

This work was undertaken at the suggestion of Professor Edmund H. Miller, and carried out under his supervision and guidance.

I take this occasion, therefore, to express my appreciation to him for his advice as well as the kind assistance which he has rendered during the work.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, January 23rd, 1903.

Prof. S. P. Thompson, President, in the Chair.

A paper "*On an Oscillating Table for Determining Moments of Inertia*" was read by Mr. W. H. Derriman.

The apparatus consists of a circular wooden table which can be suspended from a wire by means of brass supports. A pointer is attached to the centre of the bottom of the table, and immediately below is another fixed pointer. In the top of the table a circular groove is cut, in which pieces of lead can slide. These pieces of lead form together half of a circular ring of rectangular cross section. The body, the moment of inertia of which is required, is placed in position on the table and the lead weights moved until the two pointers are opposite to one another. The table therefore always oscillates about the same axis, and since the lead weights are at a fixed distance from this axis the moment of inertia of the table remains constant. The apparatus can be employed for determining the moment of inertia of a body about any axis, and is useful for proving the law that the moment of inertia of a body about any axis is equal to its moment of inertia about a parallel axis through its centre of gravity together with the moment of inertia of the whole mass, collected at its centre of gravity, about the given axis. An experipental verification of this law is given in the paper, the values of d^2 being plotted against the corresponding values of l^2. The results are correct within about 3 per cent, and the points fall upon a straight line. The moment of inertia of the table itself can be found with the aid of a body of known moment of inertia, or it can be obtained from a series of observations upon any body placed at different positions on the table.

Mr. Skinner described an inertia balance by means of which moments of inertia can be determined without the use of stop-watches. The table which carries the body is suspended by a wire. Fixed to the centre of the bottom of the table there is another wire, similar to the first, but twice as long. This wire carries a screwed brass bar, the axis of the bar being at right angles to the wire. At the middle point of this wire there is a pointer fixed at right angles to it, and on the brass bar are two weights which can be placed at varying distances from the axis. To the bottom of the bar is attached a fourth wire, the same length as the first one, and its lower end is clamped. By arranging so that the upper table oscillates to the left when the bar is oscillating to the right, and adjusting the weights on the brass bar until the pointer is stationary, the moments of inertia of bodies placed upon the table can be determined.

The Chairman referred to an inertia table designed by Prof. Perry in which an aluminium ring was supported by a trifilar suspension.

A paper entitled "*Note on an Elementary Treatment of Conducting Networks*," by Prof. L. R. Wilberforce, was read by Mr. Derriman.

In this paper the author shows that the well-known reciprocal relations between the parts of a conducting network can be readily established without an appeal to the properties of determinants. The fact that there is no continuous accumulation of electricity at any point gives a series of equations of a certain type, and the application of Ohm's law to every branch of the network gives a second series of another type. These equations are written down for two different sets of external currents and internal electromotive forces, and a general equation is obtained from which the ordinary reciprocal relations follow as particular cases.

Mr. T. H. Blakesley said the results were well known and were proved by Maxwell by a more complicated method. He pointed out that if any two conductors in a network are considered, then the rest of the network can be replaced by four suitable resistances joining the ends of the two conductors.

A paper "*On the Theory of the Quadrant Electrometer*" was read by Mr. G. W. Walker.

For the purpose of some experiments which the author is taking up he has found it necessary to examine carefully the theory of a symmetrical quadrant electrometer, and the results of his investigations are put forward in this paper. The late Dr. John Hopkinson pointed out the imperfection of the usual formula given by Maxwell, and also gave an empirical formula which closely represented his experiments. The general result is well known, namely—that the sensibility of the electrometer rises to a maximum as the potential of the needle is raised, and that any further increase in the potential of the needle reduces the sensibility. The author's experiments have been made with a sensitive electrometer by Bartels, of Göttingen, which shows a maximum sensibility when the potential of the needle is about 100 volts. The sensibility seems to go on diminishing after this, at least until very high voltages are used. The formula for a quadrant electrometer is investigated more rigidly than in the text-books, and an equation is arrived at which is practically identical with the empirical formula of Hopkinson, and which represents exactly the results obtained by the author from a Bartels' electrometer. The equation contains a constant which must be positive to explain the results, and it is shown that this is the case. An investigation is then undertaken to obtain a numerical value for this constant. The solution of the electrical distribution for a system like the quadrant electrometer is very difficult, but the author discusses and solves a similar two-dimensional problem which confirms his view that the air-gap is sufficient to account for a maximum sensibility depending upon the potential of the needle. The ordinary formula would be more nearly obeyed with a small air-gap. It is pointed out that, although diminishing the air-gap raises the potential of maximum sensibility, it does not follow that higher sensibility is obtained by reducing the air-gap. The author then discusses the results obtained by Ayrton and Sumpner from a White electrometer with a bifilar suspension, in which the variation in sensibility is shown to be due to want of symmetry. He states that this effect is not the same as that observed by Hopkinson, and that their experiments probably apply to an extremely unsymmetrical instrument of comparatively low sensibility, and that the maximum considered in this paper is beyond the range of their instrument.

Mr. Addenbrooke stated that he had studied the quadrant electrometer from a practical point of view for

many years. He looked upon Hopkinson's paper read before the Physical Society in 1885 as the basis of all work upon the electrometer. Hopkinson pointed out that in a White instrument the deflection was proportional to the potential-difference between the needle and the quadrants up to certain voltages, and ascribed the variations in sensitiveness at high voltages to want of symmetry. Mr. Addenbrooke said that there were many things which might affect the rule that the sensibility was proportional to the potential of the needle. The field is not uniform between the quadrants, the tilting of the needle may be serious, and there may be lateral displacement if the needle is not centrally suspended. In practice the distance between the quadrants must not be too small, and the needle should be as heavy as possible. He thought that the sensitiveness of different electrometers similar to the one used by the author in his experiments would vary considerably. There was always a difficulty with regard to contact-errors when working with very sensitive electrometers, but it was generally possible to get rid of it by balancing. He pointed out how the formula usually employed with a quadrant electrometer could be simplified by arranging so that the potential of one set of quadrants was as much above zero as that of the other set was below.

Mr. Appleyard said that the sensibility of the instrument was increased by doing away with the sulphuric acid and connecting wire. The effect of the surface-tension in the White electrometer was variable, and depended among other things upon the strength of the acid.

Dr. A. Griffiths indicated an improved method of arriving, in an elementary manner, at the ordinary formula for the quadrant electrometer by considering the electrical energy per unit volume instead of the capacity per unit length.

The Society then adjourned until February 13th, when the Annual General Meeting will be held.

NOTICES OF BOOKS.

A Research on the Eucalypts, especially in regard to their Essential Oils. By Richard T. Baker, F.L.S., and Henry G. Smith, F.C.S. Sydney: W. A. Gullick. 1902. Pp. 295.

With most English readers the word *Eucalyptus* does not cover a very wide field; we think of the "Blue Gum" and the "Red Gum" trees, not knowing that these are simply two species of an enormous family. In this volume the authors have divided the Eucalypts into seven principal groups and 110 species, besides varieties, all of which are probably descended from the original prehistoric *Angophora*. The authors point out that the comparative constancy of the specific characters among the Eucalypts is only what might be expected, when it is assumed that the continent of Australia is one of, if not the oldest, on the earth, having evidently remained stationary during certain subsidences and upheavals of other parts of the earth, and so preserved the fauna and flora of past geological times. During the enormous period thus represented, the species have differentiated materially from the parent stock, but the variations are comparatively few when the extensive range of the gums is considered.

With the exception of about half-a-dozen all the Eucalypts enumerated in this work will be found to possess comparatively constant botanical characters throughout their geographical distribution.

The bulk of the volume is taken up with the systematic description of the species and their essential oils; the sequence of the species is based on both botanical and chemical results, and on page 273 there is a table giving the average yields of oil obtained from the several species of Eucalypts during this research. It appears that the variation in the amount of oil in the leaves of any species of *Eucalyptus* is more largely due to the season of the year than to external conditions of rain or other weather; the largest amount is obtained in the spring time, but it has been found that in those species giving an oil rich in eucalyptol, this oil becomes richer in that constituent as the oil decreases in amount. The increase in yield is due largely to the increase in the terpenes, such as pinene and phellandrene, and it appears to be conclusive that as the year progresses the constituents first formed, in some species, change their character and tend toward the formation of eucalyptol. Nearly 500 distillations were made on an aggregate amount of nearly forty tons of leaves, and the average yield per 1000 lbs. of leaves varied from 33 lbs. 15 ozs., or 3·393 per cent in the case of the *Eucalyptus amygdalina*, to 1 oz., or 0·008 per cent, for the *Eucalyptus rubida*.

Other tables give the solubilities of the crude eucalyptus oils in alcohol, and the aggregate results of the crude oils of the various species.

The value of a research of this magnitude is very considerable, and the authors are to be congratulated on the success they have already achieved, but, as they point out in the preface, there is still a great deal more to be done.

The book is adorned with a number of excellent plates, many of them being from original drawings by Mr. R. T. Baker.

Secondary Batteries: their Theory, Construction, and Use. By E. J. Wade. London: *The Electrician* Printing and Publishing Company, Ltd. 1902. Pp. 492.

Gaston Planté was the first to investigate polarisation phenomena with a view to their utilisation rather than their elimination, his researches in this direction dating back to the year 1859. As a result of his investigations he produced a more or less practical storage battery, but it was not until 1881, when M. Faure brought out his patent for using oxides or other salts in the manufacture of the plates, that the storage battery took a commercial form.

Storage batteries as used at present are the same in principle as the original Planté cells, the only difference being in the improvements effected in the details of construction, and the methods of manufacture and treatment.

There have been, however, numerous attempts to bring into practical shape other combinations than the lead/lead-peroxide cell, with a view to getting greater storage capacity in proportion to their weight, but of these only the zinc/lead-peroxide acid cell, and the zinc/copper-oxide alkaline cell have gone so far as to be tested on a large scale, and they have been abandoned hitherto owing to their instability and rapid deterioration. A number of these cells are described in Chapter III., and though it is interesting reading no really practical results have yet been achieved.

The succeeding chapters deal entirely with lead cells, their properties and behaviour, their chemistry, their design and manufacture, their treatment and testing, their erection, connecting up, and regulation; in fact, all the information there is with regard to storage batteries seems to be included in this volume, and we most cordially commend it to all those whose work or interest lies in this direction.

Perhaps the most important chapter is No. X., on "Present-day Cells"; among these will be found the "E.P.S.," the "Crompton-Howell," the "Chloride" (both English and American), and many others. With regard to present-day accumulators, other than lead/lead-peroxide ones, the one most talked about is the "Edison," consisting of iron, and nickel oxide in an alkaline electrolyte; since the publication of the patent in the early part of 1901, the author states that he has not been able to obtain any further information, but its commercial application seems, he thinks, as far off as ever. The book is provided with two indices, one for the names of cells and electrodes only, and the other a general index.

OBITUARY.

Sir GEORGE GABRIEL STOKES, Bart.

By the death of Sir George Stokes, which occurred on Sunday last, February 1st, at his residence, Lensfield, Cambridge, Science loses one of its most distinguished men, whose death will be mourned in scientific circles throughout the world. Sir George Stokes was pre-eminently a mathematician, and as such he was second to none in this country.

But distinguished as he was, and with his time fully occupied, Sir George Stokes was always willing and able to extend a helping hand to those who appealed for his advice; he would patiently listen to their difficulties and then give of his best, and, further, he would not dismiss the matter from his thoughts when the first letter was answered, but would ponder over the problem presented to him, and would write a second and third letter, if necessary, until he felt that he had really given the assistance required.

During the time of his Secretaryship of the Royal Society, Sir George was also Editor of the *Philosophical Transactions* of the Society, and here again his rare ability asserted itself; he was editor in very fact, and many a paper was considerably improved and altered through his kindly suggestions, and its value greatly increased thereby.

George Gabriel Stokes was born at Skreen, county Sligo, on August 13th, 1819; he was educated at Dr. Wall's school at Dublin, and at Bristol College. Proceeding to Pembroke College, Cambridge, he eventually graduated as Senior Wrangler in 1841, and was elected to a Fellowship; this he vacated on his marriage in 1857, but was re-elected under the new statute in 1869. In 1849 he was appointed Lucasian Professor of Mathematics, and in 1852 he was awarded the Rumford Medal by the Royal Society (of which he had been elected a member shortly before), in recognition of his services to the cause of science by his discovery of the change in the refrangibility of light. In 1854 he was appointed one of the secretaries of the Society, and was elected President in 1885, and held this post until 1890.

In 1889 he was created a baronet in recognition of his services to Science; he received also honorary degrees from his own University, as well as from Oxford, Edinburgh, Dublin, Glasgow, and Aberdeen. In the year 1869 Sir George was President of the British Association at the meeting at Exeter, and in the following year he was appointed on the Cambridge University Commission.

On the death of Mr. Beresford-Hope in 1887 he was returned as one of the Members of Parliament for Cambridge University, and sat in the House until 1892.

The celebration of the jubilee of Professor Stokes took place three and a-half years ago, and though it is a fact that other professors had occupied their chairs for more than fifty years, still it was felt that no other professor had attained such world-wide distinction, and the celebration was accorded by the unanimous vote of the Senate.

Sir George Stokes was buried at Cambridge on Thursday, February 5th.

On the Blue Colour taken by certain Mushrooms of the Genus "Boletus."—G. Bertrand.—The author finds that the production of different colours has its explanation in the fact that the quinonic compound derived from boletol is itself of a reddish colour, while its metallic compounds are blue. According to his observations, the turning blue of the mushrooms necessitates the co-operation of six different factors: oxygen and boletol; laccase; manganese, which is generally present in the latter body; water, which acts both as a solvent and as the necessary hydrolysing agent; and, finally, an alkaline metal, magnesian or alkaline-earthy.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 10.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 2, January 12, 1903.

Some New Halogen Derivatives of Right-handed Benzylidene and Benzylcamphors.—A. Haller and J. Minguin.—The product formed by the addition of hydrobromic acid to benzylidenecamphor can be sharply distinguished from its isomers the benzyl-bromocamphors by the fact that phenyloxy-homocampholic acid is produced by rupture of the radicle in the former case, and in the latter case, under the same conditions, only the benzylidenecamphors are formed. The authors also find that during the action of excess of bromine on benzylcamphor the β-bromobenzyl-bromocamphors are first formed having the configuration of those benzyl-bromocamphors which, under the action of alcoholic potash, give rise to the β-bromo-benzylidenecamphors. These latter bodies by their extraordinary rotatory power are considered as benzylidenic derivatives of camphor. It is found, however, that the presence of bromine in the benzenic radicle apparently lessens to a certain extent the rotatory power. The authors are further researching on these substances.

Two Silicides of Manganese.—P. Lebeau.—The two silicides of manganese, $SiMn_2$ and SiMn, can both be obtained by the action of manganese on siliciuretted copper. The reaction may be considered as corresponding to the chemical equilibrium produced in the elementary system copper, silicon, and manganese. In a further communication the author intends to show how an investigation of these equilibriums leads to the preparation of the compounds of silicon and a metal, and how a third manganese silicide can be obtained.

Dilatation of Tempered Steel.—Georges Charpy and Louis Grenet.—In a former research the authors found the dilatation of steels having different compositions. They now continue their investigations, and by the same method find the dilatations of specimens of steel tempered under different conditions. Their experiments apparently show that the effects of tempering on the phenomena of dilatation are not affected by variations of mechanical properties or by the points of transformations indicated by the various methods. These facts seem difficult to reconcile with the theory often stated that empering acts on the properties of the steel principally by maintaining the carbon in a state of solid solution, or the iron in an allotropic state differing from the stable state in the cold. The authors' results seem to show that actions of a different order intervene.

Chloride of Cinnamylidene.—Ernest Charon and Edgar Dugoujon.—The preparation of chloride of cinnamylidene by the action of phosphorus perchloride on cinnamic aldehyde has been tried without success by Cahours, an indistillable and non-crystalline oil only being obtained. The authors once more take up this investigation to see if the chloride obtained, which ought to have the formula $C_6H_5—CH=CH—CHCl_2$, would not show the special characteristics which M. Charon has already described. The negative character of the group, $C_6H_5—CH=CH—$, is very marked in this compound. They therefore modify Cahours' preparation, and succeed in obtaining cinnamylidene chloride in a tolerably pure state.

Action of Sodium on 1.3 Iodine Phenoxypropane. Diphenoxyhexane.—J. Hamonet.—During his researches on 1.4-butanediol the author observed a peculiar reaction with certain metals on bromated or even iodated phenoxyethane. Instead of the diphenoxybutane expected, there was produced the bromide and phenate of sodium.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 12.

A New Method for the Preparation of Oxygen from Oxylith.—G. F. Jaubert.—Already noticed.

A Preparation of Gaseous Phosphide of Hydrogen.—F. Bodroux.—Already inserted.

The Complex Salts of Osmium; Osmyloxalate of Potassium.—M. Vèzes and L. Wintrebert.—Already inserted in full.

Action of Ethylic Alcohol on Ethylate of Baryta. Synthesis of Normal Butylic Alcohol. — Marcel Guerbet.—By heating a concentrated solution of ethylate of baryta in absolute alcohol to 230—240° a small quantity of normal butylic alcohol is formed, and, at the same time, ethylene, hydrogen, and acetate and carbonate of baryta. The concentrated ethylate of baryta is prepared by dissolving caustic baryta in the cold in absolute alcohol, and heating the solution to boiling-point. Ethylate of barium, which is less soluble hot than cold, is precipitated, and it suffices to decant the greater part of the supernatant alcohol to obtain a concentrated solution of ethylate of baryta. This solution is placed in sealed tubes, and heated to 230—240° for twenty-four hours three separate times. At the end of each twenty-four hours the tubes are opened to allow the gas to escape, then sealed up again. The gas thus produced is passed through a series of five wash-bottles containing successively water, bromine, solution of soda, concentrated sulphuric acid, and absolute alcohol; it is then collected over water. The bromine absorbs the ethylene, the soda the fumes of bromine, the sulphuric acid dries the gas, and the alcohol dissolves the methane which is formed by the pyrogenous decomposition of the ethylate of baryta; the residual gas is hydrogen only. The contents of the sealed tubes are distilled on an oil-bath to dryness; the distillate is rectified, and passes over between 76° and 130°; after rectifying a large number of times, a small quantity of liquid is separated at length, boiling at 115—117°; this is normal butylic alcohol, $C_4H_{10}O$.

Action of Normal Propylic and Butylic Alcohols on their Respective Soda Derivatives. Synthesis of Dipropylic and Dibutylic Alcohols.—Marcel Guerbet.—Already noticed.

Mixed Imidodithiocarbonic Ethers. — Marcel Delépine.—Already noticed.

Action of the Halogen Ethers on the Sulphocarbonic Compounds of the Secondary Amines.—Marcel Delépine.—Already noticed.

The Variation of the Rotatory Power of the Ether Salts of the Stable levo-borneol.—J. Minguin and E. Grégoire de Bollemont.—Already noticed.

Condensations with Zinc and Iodacetate of Ethyl.—L. Téry.—The author has examined the reactions of iodacetate of ethyl on various substances in the presence of zinc; with β-methylcyclohexanone he obtained methylcyclohexanolacetate of ethyl; with pulegon he obtained pulegol acetate of ethyl, $C_{14}H_{24}O_3$; with citral, citralidene acetate of ethyl, $C_{14}H_{22}O_2$, from which he obtained citralidene acetic acid, $C_9H_{15}—CH=CH—COOH$, very easily by saponifying with alcoholic potash. After saponification there remains an alkaline solution which is shaken up with ether, in which a substance with a strong aromatic odour, resembling sandal-wood, is slightly soluble.

Some Reactions of Fenone.—E. Tardy.—Fenone is capable of forming numerous molecular compounds, notably with the phenols. These compounds are exothermic, and the reaction has the effect of increasing the rotatory power; the most interesting of these compounds are the naphthofenones, bodies which are perfectly crystallised. Another property of fenone is that it dissolves nitrocellulose. A mixture of 1 part of nitrocellulose and 2 parts of fenone forms a gelatinous mass; 10 per cent of fenone in alcohol will dissolve gun-cotton, giving a kind of collodion.

Action of Isocyanate of Phenyl on the Ethers of some Oxyacids. — E. Lambling. — The author has examined the action of isocyanate of phenyl on α-oxybutyric ether, on normal α-oxyvalerianic ether, and on α-oxyisovalerianic ether, and gives the results of his experiments in detail, with the analysis of the products obtained.

Some Salts of Antipyrine.—A. Reychler.—When we evaporate an aqueous solution of antipyrine, treated with a slight excess of hydrochloric acid, a syrupy residue is obtained showing hardly any signs of crystallisation. To obtain a better result, 30 grms. of antipyrine, 50 c.c. of alcohol, and 20 c.c. of strong hydrochloric acid were concentrated on the water-bath; the residue was treated with a further quantity of alcohol and acid, and re-evaporated; the mass formed was eventually freed from moisture by washing it with alcohol and ether, and, finally, with pure ether; the body formed is chlorhydrate of antipyrine, $C_{11}H_{12}ON_2.HCl$; it is barely soluble in benzene, but fairly so in a boiling mixture of 5 parts of benzene to 1 part of absolute alcohol. On cooling, an abundant crop of prismatic crystals is obtained, containing benzene of crystallisation. The author has also prepared the camphorsulphonate of antipyrine; it is very soluble in water though not deliquescent; it can be re-crystallised with ease from a mixture of 1 part of absolute alcohol and 4 parts of acetone in the form of hard compact prisms, fusible at 166°.

The Acids of "Bignonia Catalpa."—A. Piutti and E. Comanducci.—The authors find that the fruit of the "Bignonia catalpa" gathered when unripe does not contain $C_{14}H_{14}O_3$ (Sardo's catalpic acid), but *p*-oxybenzoic acid and the compound of *p*-oxybenzoic and protocatechuic acids.

The Estimation of Urea in Urine.—Ch. Sallerin.—The author has compared various methods, and finds amongst other things that Braunstein's method with the hydrolysis of the urea for seven hours at 150—155° is the best, and he used it to check the accuracy of other more simple methods.

Microchemical Analysis of some Alkaloids.—M. Surre.—Not suitable for abstraction.

Estimation of Glycerin by means of Iodic Acid in the presence of Sulphuric Acid.—A. Chaumeil.—Inserted in full.

The Conditions in which the Starch exists in New Bread and in Stale Bread.—M. Lindet.—The alimentary examination of bread has been devoted, up to the present, rather to the gluten than the starch, though it is more from the state in which the starch exists that we should expect to obtain information as to its assimilation. Under the influence of the moist heat of the oven the starch undergoes all conditions of gelatinisation down to that of soluble starch or amylodextrine. The insoluble portion is partially soluble, however, in very dilute hydrochloric acid, also in the form of amylodextrine, from which it is possible to determine the degree of gelatinisation. With regard to the actual composition of new and stale breads, the author gives a number of analyses which show that the composition of the crust is invariable; the amount of dextrine is greater than in the crumb; the starch is broken down, but is not even partially soluble in dilute acid. On the other hand, there are many transformations in the crumb. The weight of soluble dextrines is as much as 10 per cent in bread just leaving the oven; this weight diminishes progressively on keeping until it reaches only 2 per cent after forty-eight hours; it is the amylodextrine that has retrograded.

MISCELLANEOUS.

The American Electro-chemical Society.—In the last number of the CHEMICAL NEWS (vol. lxxxvii., January 30th, 1903) we announced the proposed formation of a Society of Electro-Chemists and Metallurgists: in this connection we may mention that we have received since then a pamphlet setting forth the preliminaries connected with the formation of the "American Electro-chemical Society." The first meeting was held on November 1st, 1901, at the Engineers' Club, Philadelphia, and as a result of this meeting the first general meeting of the proposed Society was called for April 3rd, 4th, and 5th, 1902, at Philadelphia, and Committees were appointed to enrol members and secure papers. At the meeting on April 3rd the Society was organised under the Presidency of Professor Joseph W. Richards, Ph.D., while a number of distinguish scientific Americans filled the offices of Vice-Presidents, Board of Managers, Secretary, and Treasurer. On Friday, April 4th, a number of papers were read and discussed, of which one of the principal ones was entitled "A University Course in Electro-chemistry," by Professor Richards. The author went over the ground already covered by the courses in chemistry, metallurgy, and electrical engineering, and pointed out where they would and would not be satisfactory as a preparation for the course in electro-chemistry. He is of the opinion that such a course must contain thorough drill in the fundamental principles of both chemistry and electricity, and a full treatment of the borderland between the two sciences, which is the special province of electro-chemistry as a pure science. This end is best attained by starting with the course in metallurgy and modifying it so as to include the fundamentals of electrical engineering, and adding thereto lectures and laboratory work in specific electro-chemical subjects. It is probable that a course thus constructed will be found not only to meet the practical needs of the student wishing to enter the electro-chemical industries, but also that it will possess a high educational value.

The Pentachloride, Pentabromide, and Pentaiodide of Antimony and their Double Salts.—A. Rosenheim and W. Stellman.—Pentachloride of antimony in solution in absolute alcohol when treated with hydrochlorate of pyridine, cooled down to 0°, and then treated with gaseous hydrochloric acid, gives beautiful reddish brown needles of chlorantimoniate of pyridine, $3C_5H_5NHCl.2SbCl_5$; in the same manner we can obtain the corresponding compounds of quinolein and dimethylaniline, in beautiful white crystals. The pentabromide of antimony, $SbBr_5$, has not yet been isolated, but if ether is cooled and kept in the dark and saturated with HBr gas, then treated with antimonic acid, a brown solution is formed which, if treated with bromhydrate of pyridine in alcoholic solution, gives black crystalline flakes of a bromantimoniate, $2C_5H_5NHBr.SbBr_5$; these can only be re-crystallised by adding an excess of bromine and re-cooling, otherwise we obtain yellow needles of a bromantimonite, $2C_5H_5NHBr.SbBr_3$. Analogous results are obtained with quinolein, &c. Antimonic bromide combines with a very large number of organic substances; we operate in the presence of chloroform, which enables us to obtain the products unchanged in a crystalline form; with aldehyde we obtain $SbCl_5.C_2H_4O$, in yellowish white needles; with benzylic aldehyde $SbCl_5.C_6H_5COH$, in needles; with acetone $SbCl_5.CH_3COCH$, in prisms; with chloride of benzoyl $2SbCl_5.3C_6H_5COCl$, in needles; with benzoate of ethyl $SbCl_5.C_6H_5CO_2C_2H_5$, in rhombic tables; acetamide gives $2SbCl_5.3CH_3CONH_2$; phthalic anhydride $2SbCl_5.3(CH_4[CO]_2O)$; with oxalic acid we get $2SbCl_5.C_2O_4H_2$ in prisms. It is necessary to take 2 molecules of $SbCl_5$; with only one we should get a different reaction. Succinic acid gives $2SbCl_5.C_4H_6O_4$ in fine needles, and nitrobenzene gives $2SbCl_5.3C_6H_5NO_2$. The carbides do not unite with $SbCl_5$ without alteration; with benzene there is a reduction to the state of trichloride and the formation of $3SbCl_3.C_6H_5$, in large prisms.—*Ber.*, xxxiv., 3377.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., Sir James Crichton-Brown, Treasurer and Vice-President, in the Chair. The following were elected Members:—Dr. Louisa Garrett Anderson, Dr. Henry T. Böttinger, Mr. W. Child, Mrs. Ionides, Miss E. Lee-Smith, Sir Frederick Treves, Bart., and Mr. W. Whitehead.

Institute of Chemistry of Great Britain and Ireland.—Pass List of the January Examinations.—Of twelve candidates who entered for the Intermediate Examination, the following eight passed:—D. B. Byles, B. F. Davis, A. V. Elsden, James Gray, Arthur Hopwood, J. R. Johnson, W. O. Littlebury, and H. Stevenson. In the Final Examination for the Associateship (A.I.C.) in Mineral Chemistry, of eight who entered the following six passed: K. B. Benham, A. E. Case, B.Sc., G. F. D. Green, T. B. Kirkhope, M. W. Stevens, Assoc.R.C.Sc., and James Thorburn; one candidate passed in Physical Chemistry: J. Johnston; in Organic Chemistry, of the eleven who entered the following seven passed: H. W. Bywaters, Assoc.R.C.Sc., Ph.D., H. Finnemore, R. J. Hall, B.Sc., F. T. Jewson, S. G. Paine, J. B. Pursglove, and H. A. Tempany, B.Sc.; of six who entered in the branch of the Analysis of Food and Drugs, and of Water, including the examinations in Therapeutics, Pharmacology, and Microscopy, the following five passed: W. L. St. J. Alton, J. C. Gregory, B.Sc., E. K. Hanson, B.A., F. E. King, B.Sc., and A. W. Knapp, B.Sc. The Examiners in Chemistry were Dr. Bernard Dyer and Professor W. Palmer Wynne; Dr. Arthur P. Luff conducted the examination in Therapeutics, Pharmacology, and Microscopy.

MEETINGS FOR THE WEEK.

MONDAY, 9th.—Society of Arts, 8. (Cantor Lectures). "Paper Manufacture," by Julius Hübner.

TUESDAY, 10th.—Royal Institution, 5. "The Physiology of Digestion," by Prof. Allan Macfadyen, M.D.

—— Society of Arts, 5. "Women in Canada," by the Countess of Aberdeen.

WEDNESDAY, 11th.—Society of Arts, 8. "The Port of London," by B. W. Ginsburg, M.A., LL.D.

THURSDAY, 12th.—Royal Institution, 5. "Arctic and Antarctic Exploration," by Sir Clements Markham, K.C.B., F.R.S.

FRIDAY, 13th.—Royal Institution, 9. "Health Dangers in Food," by Prof. Sheridan Delépine, M.B., B.Sc.

—— Physical 5. Annual General Meeting. Address by President elect.

SATURDAY, 14th.—Royal Institution, 3. "Dramatic Criticism," by Arthur B. Walkley.

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THE CHEMICAL NEWS.

VOL. LXXXVII., No. 2255.

REVISION OF THE ATOMIC WEIGHT OF LANTHANUM.*

By BOHUSLAV BRAUNER, Ph.D., and FRANTIŠEK PAVLÍČEK, Bohemian University, Prague.

(Continued from p. 64).

Second Method of Atomic Weight Determination. Analyses of Lanthanum Sulphate. New Hydrate of Lanthanum Sulphate.

CONVERSION of the anhydrous sulphate into the oxide by calcination was the method used by Marignac, in 1873, who obtained in this way La=138·81 (see Table I.), and the same method was used later on with scandium, thorium, and cerium (Nilson, Krüss, Brauner).

The residues from the above two series of experiments were purified from alkali, &c., in the manner already indicated, and the anhydrous sulphate of lanthanum was prepared. It was dissolved in five to six parts of ice-cold water in a platinum dish plunged in ice, but instead of crystallisation being effected by heating to 35—40° (Mosander, Bunsen), the ice-cold solution was stirred until the hydrated salt had separated out, after which it was allowed to assume the ordinary temperature.

The salt was collected by suction on a perforated platinum plate, washed well with cold water, and dehydrated at 500—600°. By repeating this process of recrystallisation ten times, the fractions P 1 to P 10 were obtained from the original sulphate P.

During these experiments, in which I was aided by Mr. Picek, we observed that the proportion of the sulphate remaining in the filtrates was not always the same, and, similarly, the character of the sulphate was different. The sulphates P 4, P 6, P 7, and P 10 consisted of fine needles, others formed distinct prismatic crystals resembling the enneahydrate.

The salt P 4 was especially characteristic as forming flocks like alumina, consisting, however, of the finest needles. It separated out at 0—1°; it was quickly collected on the pump, pressed between smooth paper, and the dry powder immediately weighed in a closed platinum crucible.

Experiment 28.—1·93822 grms. of the salt P 4 gave, on drying at 500°, a residue of 1·28710 grms. and on further drying for eight hours at 550° ±, of 1·28663 grms. of the anhydrous salt, from which it is seen that lanthanum sulphate parts only with great difficulty with the last traces of its water of crystallisation. The loss of weight, which in this case can only be due to loss of water, was 0·65159 grm., or 33·618 per cent, which is equivalent to 15·92 molecules.

The remaining 1·28663 grms. of the anhydrous sulphate were very gradually heated to a yellow heat, and yielded 0·74122 grm. of La_2O_3=57·6103 per cent. From this, La=139·207.

In order to ascertain whether the weight of the oxide remained constant, the product was heated again for one hour over the blowpipe. Its weight became 0·74153 grm.; that is, it became heavier by 0·0003 grm. On further heating, the weight decreased to the minimum of 0·74123 grm. (compare Experiment 29).

It is evident from the above that the hydrated salt analysed is a new hydrate of lanthanum sulphate, the *hekkaidekahydrate.*

		Calculated.		Found.
La_2O_3	.. =	326·17 (*a*)	38·17	38·24
$3SO_3$	.. =	240·18	28·10	28·14
$16H_2O$	.. =	288·24	33·73	33·62
		854·59	100·00	100·00

(*a*) The atomic weight "in air" is used here.

Muthmann and Rölig (*Ber.*, 1893, xxxi., 1723) say that the enneahydrate ($+9H_2O$) is formed at all temperatures, and that they endeavoured in vain to obtain another hydrate, so that the existence of the new hydrate is not devoid of interest. (The hexahydrate crystallises only from an acid solution).

Mr. Picek tried to determine the solubility of the hekkaidekahydrate and its transition temperature into the enneahydrate, but we only learned that the system, hekkaidehydrate + water, is a very labile one, even at a temperature near 0°.

For a second experiment, the salt P 10 was used. It undoubtedly originally consisted chiefly of the hekkaidekahydrate; it was well drained on the pump and kept in a covered platinum dish. Next day it was found to be very moist and converted completely into the enneahydrate.

Experiment 29.—1·96466 grms. of the air-dried salt gave 1·51969 grms. after heating for ten hours at 530°, and, after further drying for six-and a-half hours at 600° ±, 1·51947 grms., showing that the last 0·00022 grm. of water was retained very strongly. The loss of weight, 0·44519 grm., amounts to 22·66 per cent, the calculated amount for $9H_2O$ being 22·26 per cent.

On raising the temperature gradually to the highest yellow heat obtainable with the blowpipe, this salt was found to lose its sulphuric acid with great difficulty, and all attempts to obtain an oxide of a constant weight were fruitless:—

Time of heating.	Weight of residue in grm.	Apparent atomic weight of La.
Half-day over the blowpipe ..	0·95751	180·6
Half-day „ „ ..	0·87937	140·9
One day „ „ ..	0·87521	139·192
Eight and a-half hours over the blowpipe	0·87649	139·70
Ten minutes at yellow heat ..	0·87586	139·43
Two hours over the blowpipe ..	0·87645	139·68
Quarter hour at almost white heat	0·87571	139·36

In the last instance, the temperature was so high that the two crucibles were nearly soldered together.

It is seen from Experiments 28 and 29 that the above simple method, which gives excellent results with such weak bases as CeO_2 and ThO_2, cannot be used with the strong base La_2O_3. But even when the minimum weight was reached by a chance, the oxide was heavier by 0·00012 grm. than required by theory. T. W. Richards has found that oxides obtained from the sulphates "occlude" a larger quantity of gases than those obtained by heating the oxalates. Lanthanum oxide obtained from the oxalate is voluminous and almost white, that obtained from the sulphate is denser and greyish-buff in colour.

The fact that after ten re-crystallisations from its aqueous solution the sulphate is perfectly normal and not even slightly basic, shows that the amount of its hydrolysis in a cold aqueous solution of the above concentration must be quite inappreciable.

Experiment 30.—This shows that on heating lanthanum sulphate to the highest temperature obtainable with a Bunsen burner (without blast) it loses easily two-thirds of its SO_3, and a new basic sulphate La_2O_3,SO_3, stable at a higher temperature, is obtained.

4·0867 grms. of the anhydrous sulphate, obtained by synthesis from 2·3535 grms. of the oxide, yielded, when heated as above, a residue weighing 3·2044 grms., which when heated to a still higher temperature decreased to

* From the *Transactions of the Chemical Society*, 1902, vol. lxxxi.

2·9146 grms. of the basic sulphate. From this, SO_3 = 0·5611 grm., an amount approaching that required for $1SO_3$ = 0·5777 grm. An analogous phenomenon was observed by me in the case of praseodym sulphate.*

The above two experiments show that the true atomic weight of lanthanum cannot lie higher than 139·20 (in air) or 139·14 (in a vacuum). No indication of a "lanthanum" with the low atomic weight 135 was found in our purest lanthanum material.

(To be continued).

THE METALLIC NATURE OF HYDROGEN.

By GEOFFREY MARTIN, B.Sc.(Lond.).

One of the most remarkable facts in chemistry is the two-fold nature of hydrogen. On the one hand, it behaves precisely as a metal in a vast number of its chemical relations; and on the other hand, it exhibits equally decided non-metallic characteristics.

Its metallic properties are striking in the extreme:—

1. It generates a whole series of salts—the so-called acids—which are perfectly analogous to the corresponding compounds of Na and K, except in so far as they are stamped with the peculiarities of hydrogen itself. Such compounds, for example, are capable of electrolytic dissociation, the H playing precisely the same part as a Na or K ion.

It was such facts as these, as well as the other special chemical relations of combined H, that forced the great chemists of the preceding century—Faraday, Dumas, Daniell, Graham, and Andrews—to entertain the view that H was metallic in nature, and allied to K or Na.

2. When hydrogen enters into the structure of a compound it exercises the same effect on its properties as a light metal, such as Na or K, making in general an acid compound less acid, and a basic compound more basic.

For example, phenol, $C_6H_5.OH$, is more acid in nature than hexylic alcohol, $C_6H_{13}.OH$; and benzoic acid, $C_6H_5.COOH$, is more acid than hexylic acid, $C_6H_{13}.COOH$.

Similarly, N_3H is an acid, but N_2H_4 and NH_3 are strong bases.

The same effect is produced by Na or K. For instance, H.OH is neutral, but H.ONa a strong base. The diminution of acidity which follows the replacement of H by Na is well seen in the malonic esters:—$HOOC-CH_2-COOH$, $HOOC-CHNa-COOH$, $HOOC-CNa_2-COOH$.

3. When the elements are arranged in the order of their affinity for positive electricity (Nernst, Newman), H actually occurs among the metals, between lead and tin, as the following series shows:—Mg, Al, Zn, Cd, Fe, Co, Ni, Pb, H, Sn, Cu, Hg, Pd, Au (Newman, *Zeit. f. Phys. Chem.*, 1894, xiv., 193, particularly pp. 222—223; *vide* also Nernst, *Ber.*, 1897, xxx, 2, 1547).

So that H is able to precipitate from their solutions such metals as Cu, Hg, Ag, Pt, Au_4 in just the same way that Mg precipitates such metals as Zn or Cd.

This may be easily shown experimentally by immersing a small plate of Pd, saturated with H, in a solution of $CuSO_4$. The plate soon becomes covered with a lustrous layer of Cu (Lüpke's "Electro-chemistry," 1897, p. 166).

4. Moreover, the thermal effects produced by the combination of H with equivalent quantities of the successive elements P, C, S, N, O are in the same order as those produced by the combination of Na with the same substances. Whereas the order in the case of a non-metal, such as chlorine, is diametrically opposite (van't Hoff "Lectures," iii., 93).

5. In addition, Pd is able to absorb several hundred times its volume of H gas and still retain its lustre and general metallic appearance, as would be the case if the compound is a Pd-H alloy.

From these facts it will be seen that H in its chemical relations presents all the characteristics of a metal.

On the other hand, Dewar has shown that liquid hydrogen is quite non-metallic in nature, being a non-conducting, transparent, mobile liquid, resembling, in fact, a liquid hydrocarbon rather than a metal.

How then are we to reconcile this sharp contrast between the chemical and physical nature of H?

For it is indisputable that H at ordinary temperatures behaves as a metal in most of its chemical relations.

While it is equally indisputable that at a very low temperature, at its boiling-point for example, hydrogen possesses the properties of a non-metal.

Is not the solution of this riddle to be sought in my suggestion (Chemical News, 1902, lxxxvi., 295) that a high temperature tends to bring out metallic properties, and conversely, a low temperature to bring out non-metallic properties, so that, although at ordinary temperatures and pressures H shows a marked inclination to exhibit the fundamental properties of a metal, yet, nevertheless, at −252·5° (its boiling-point) its metallic properties have entirely disappeared?

The idea is well worthy of consideration, inasmuch as it affords a very simple explanation of one of the otherwise most inexplicable facts in chemistry.

University of Kiel, January 22, 1903.

ACTION OF HYDROCHLORIC ACID ON THE SULPHATES OF THE SESQUIOXIDES OF ALUMINIUM, CHROMIUM, AND IRON.

By A. RECOURA.

When the salts of the sesquioxides of aluminium, chromium, and iron are dissolved in water they undergo a partial decomposition, especially when heated, and this has the effect of liberating a portion of the acid of the salt. On the other hand, it is probable from what we know of these compounds that the three hydroxyls of the bases, $Al(OH)_3$, $Cr(OH)_3$, and $Fe(OH)_3$, are not identical, and that some of them are able to change their functions under certain circumstances, as M. Wyrouboff has shown very plainly in his paper on the "Constitution of the Compounds of Chromium" (*Bull. Soc. Chim.*, Series 3, vol. xxvii., p. 666).

Under these circumstances it became interesting to try how the solutions of these salts would behave when acted on with a different acid to that in the salt, and one of less energy. Thus, for example, the sulphate of sesquioxide of chromium dissolved, losing, as I have already shown, under the action of heat, a portion of its sulphuric acid, which is set free; it was probable that if this decomposition took place in the presence of another acid more feeble than sulphuric acid, such as hydrochloric acid, for example, used in considerable excess, the base or the hydroxyls of the base liberated by the separation of the sulphuric acid, might fix one or more molecules of hydrochloric acid, and thus give rise to the formation of a polyacid salt in which the hydroxyls of the base would become saturated, some with the sulphuric acid, and the others with the hydrochloric acid.

Experiment has verified these suppositions. I am now about to give the results I have obtained by acting in hot solution with hydrochloric acid on the sulphates of aluminium, chromium, and iron.

With the sulphates of aluminium and chromium I obtained, as I expected, polyacid salts, $Al.SO_4.Cl.6H_2O$ and $Cr.SO_4.Cl.6H_2O$, while with sulphate of iron I transformed this sulphate, $Fe_2,3SO_4$, into an acid sulphate, $Fe_2,3SO_4.SO_4H_2.8H_2O$.

I will describe first the chromic compound, which has very interesting properties.

* This fact was communicated to the Chemical Society on Feb. 24, 1902. Later on (*Comptes Rendus*, 1902, cxxxiv., 657), basic sulphates of Pr and Nd of the same formula, R_2O_3,SO_3, were described by Matignon. My discovery was made independently of that author.

Chlorosulphate of Chromium, $Cr.SO_4.Cl.6H_2O$.—This compound is obtained easily in the following manner:—To 50 c.c. of fuming hydrochloric acid brought to the boiling-point, we add 60 grms. of the violet sulphate of chromium, which dissolves immediately, giving a green liquid. Boil for a quarter of an hour, and let the solution stand. After the lapse of several days a mass of crystals is formed, which is drained as thoroughly as possible, and then washed with a mixture of alcohol and acetone. Thus we obtain a green powder very soluble in water, and to which analysis gives the formula $Cr.SO_4\,Cl,6H_2O$. (Found—Cr, 1; SO_4, 1·003; Cl, 1·001; H_2O, 5·95).

It should be remarked that in this compound we find the 6 molecules of water that exist in the two chlorides of chromium, the green chloride and the violet chloride, which have both the composition $CrCl_3\,6H_2O$. These 6 molecules of water are water of constitution, as I shall show further on; the loss of a single one of these molecules modifies the properties of the body considerably. It should be remembered that while the green chloride of chromium is soluble in alcohol and in acetone, this compound is insoluble therein. I would add that we must give it the molecular formula $CrSO_4Cl$, and not a double or triple formula, since this is required by the cryoscopic measurements given later on.

The most interesting property of this body is the following:—The chlorine it contains is not precipitated by nitrate of silver, while the whole of the sulphuric acid is precipitated immediately by chloride of barium. The experiment should be made in the following manner:—To a dilute solution (1 molecule to about 35 litres) freshly made, cooled to 0°, and acidulated with nitric acid, we add the equivalent quantity of nitrate of silver. The solution remains perfectly limpid for more than a quarter of an hour, then it becomes cloudy, and gradually a precipitate is formed. If we operate at the ordinary temperature and without the addition of nitric acid the precipitation commences almost immediately. For, like all the complex compounds of chromium that I have described, and in which the acid radicles are masked, this one is transformed fairly rapidly by water. Thus, after a certain time, the solution of this body, which is green at first, changes to violet, and it is then no longer anything more than a *mixture* of the violet chloride and the violet sulphate; this can be verified easily by cryoscopy.

A recently made solution, containing 3·564 grms. of chlorosulphate of chromium in 100 grms. of water, congeals at −0·29°. The same solution kept for six days, and become violet, congealed at −0·42°. Now, the corresponding quantities of the violet sulphate and the violet chloride produce, at the same dilution, lowerings of temperature which are respectively 0·16° and 0·26°, and of which the sum is 0·42°. Thus, it is seen easily that the solution of the chlorosulphate of chromium, after it has become violet, is nothing but a mixture of the sulphate and the chloride.

Chlorosulphate of Chromium, $Cr.SO_4.Cl,5H_2O$.—The preceding salt, which contains 6 molecules of water when kept at a temperature of 85°, gradually loses water, and we observe that when it has lost 1 molecule, its solution, when very dilute (1 molecule in 500 litres), which previously was precipitated by chloride of barium, no longer has that property, all other conditions being the same. Neither is it precipitated by nitrate of silver. Thus the loss of 1 molecule of water has the effect of making the sulphuric acid enter the complex radicle which already contains the chlorine and the chromium. If we continue to heat it, still at 85°, this compound continues to lose water and becomes more difficultly soluble, but at the same time it loses a little hydrochloric acid.

It became of interest to determine the lowering of the congelation point of the aqueous solutions of this compound. We know, as a matter of fact, that while the molecular lowering in water of non-electrolytic compounds is 18·5, electrolytes always have a much more pronounced molecular lowering, which is generally explained by their partial dissociation into their ions, caused by the water, and this has the effect of increasing the number of active cryoscopic particles. Now, the compound in question does not undergo double decomposition, so it may be presumed that it is not dissociated by water, and that it will behave like the non-electrolytes. This has been fully verified by experiment. I have found for the molecular lowering of the compound $Cr.SO_4.Cl,5H_2O$ the number 18·8; that is to say, the same lowering as the non-electrolyte; while under the same conditions of dilution (1 molecule per 10 litres) the compound with 6 molecules of water, which is dissociable, gave 23·7, and the green chloride of chromium, $CrCl_3.6H_2O$, gave 40.

It must be observed that the compound with 5 molecules of water is transformed very rapidly when it is dissolved into the compound with 6 molecules of which the sulphuric acid is precipitable. Thus, after twenty minutes solution, the molecular lowering is already brought up from 18·8 to 21·1, and the solution is precipitated perfectly by chloride of barium. But if the dehydration is pushed beyond the $5H_2O$ stage,—if, for example, the compound is made to give up 2 molecules of water,—its solution is then much more stable; the sulphuric acid is masked for a much longer period.

I shall return later on to the constitution of these compounds, and that will help to fix that of the other complex compounds of chromium, which is occupying the attention of many chemists at the present time.

Chlorosulphate of Aluminium, $Al.SO_4.Cl,6H_2O$.—This compound is prepared under the same conditions as the chromic compound. To 50 c.c. of boiling fuming hydrochloric acid we add 40 grms. of sulphate of aluminium, which dissolves immediately. Boil for a quarter of an hour; on cooling, the liquor gives an abundant crop of crystals, which are drained and then re-crystallised a second time, under the same conditions, by dissolving them in boiling hydrochloric acid. The crystals are drained carefully and then washed with acetone.

In this manner we obtain a salt which is very soluble in water, and almost insoluble in alcohol, of the composition $Al.SO_4.Cl,6H_2O$. (Found—Al, 1; SO_4, 0·999; Cl, 1·002; H_2O, 5·9).

It should be remarked that we find in this compound the 6 molecules of water that are present in chloride of aluminium, $AlCl_3,6H_2O$, in the same manner that we find the 6 molecules of water of the chromic chloride in the corresponding compound of chromium.

We may ask if the compound thus obtained is really a polyacid salt, $AlSO_4Cl$, or if it may not be a double salt, $Al_2,3SO_4.AlCl_3$, resulting from the union of a molecule of sulphate of aluminium with a molecule of the chloride. In the case of the chromic compound the properties of the body, as well as the cryoscopic measurements, leave no doubt in this respect, as has been seen.

They show that the aqueous solution of this body really contains the compound $CrSO_4Cl$ from the commencement, but being unstable this compound is gradually destroyed by the water, and that after the lapse of several days it contains nothing but a simple mixture, $Cr_23SO_4 + CrCl_3$.

In the case of the aluminic compound the cryoscopic measurements show that the solution in water, even from the first minute, is nothing more than a simple mixture of sulphate of aluminium and the chloride. In fact, the lowering of the congealing point of the aqueous solution of this compound is the sum of the lowering of the congelation points of the sulphate and the chloride it contains.* Thus, while the chlorosulphate of chromium is only destroyed slowly by water, that of aluminium is decomposed at the moment of its solution; consequently, the

* In fact, a solution containing 1 grm. of the compound in 100 grms. of water congeals at −0·50°. Now, the amounts of sulphate and of chloride they contain, produce, at the same dilution, lowerings which are respectively 0·22° and 0·30°, and the sum is 0·52°. Thus we see plainly that the solution of chlorosulphate of aluminium behaves as a mixture of the sulphate and the chloride.

examination of the solution does not enable us to solve the question of the composition of the solid compound.

But admitting that it is produced under exactly the same conditions as the chromic compound, and that it has exactly the same composition, we are justified in assuming that it has probably the same constitution; that is to say, that it is a polyacid.

Further, this opinion is confirmed by the following fact:—If the compound was a double salt we should probably obtain it by crystallising a mixture of the sulphate and the chloride dissolved in water. Now, in the crystallisation of such a mixture there is no trace of the chlorosulphate of aluminium formed; the crystals obtained are a mixture, in variable proportion, of sulphate and chloride, a mixture which, when treated with alcohol, gives up the whole of its chloride, while the chlorosulphate is undecomposed by alcohol under the same conditions.

For all these reasons we must admit that the chlorosulphate of aluminium, $Al.SO_4.Cl,6H_2O$, has the same constitution as the chlorosulphate of chromium, $Cr.SO_4Cl,6H_2O$. Now, I have shown that this body is a complex compound, that the chlorine is masked, and that in the same compound with 5 molecules of water the sulphuric acid also is masked. Therefore it is probable that the same is the case with the aluminic compound. But while we are able to prove it with the chromic compound because it is only decomposed slowly by water, we cannot do the same with the aluminic compound, since it is instantly decomposed by water.

This is the same with the whole series of complex compounds of chromium that I have examined. We can prove their properties, since, though fragile, solution in water does not destroy them immediately. It is not improbable that analogous compounds of aluminium exist; but it is probable that these compounds, like the chlorosulphate of aluminium, are destroyed very rapidly on solution.

Acid Ferric Sulphate, $Fe_2,3SO_4.SO_4H_2,8H_2O$.—We might expect ferric sulphate to form an analogous compound, but such is not the case. Under the same conditions ferric sulphate forms, not a chlorosulphate, but on the one hand ferric chloride, and on the other hand an acid sulphate, $Fe_2,3SO_4,SO_4H_2,8H_2O$. I am engaged with its examination at the present time, and will publish the results before long.

I am also making an examination of the action of the different acids on the salts of aluminium, chromium, and iron.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 23.

THE DOUBLE AMMONIUM PHOSPHATES IN ANALYSIS.*

By MARTHA AUSTIN.

The function of ammonium salts in the formation of double ammonium phosphates for the purposes of analysis has been the subject of a good deal of study. Manganese, which tends to fall as the tribasic phosphate, $Mn_3P_2O_8$ (Gooch and Austin, *Am. Journ. Sci.*, vi., 233) appears in the presence of a sufficiency of ammonium salt in the form of the ammonium manganese phosphate, $(NH_4)MnPO_4$, which gives the pyrophosphate, $Mn_2P_2O_7$, on ignition. Magnesium (Gooch and Austin, *Am. Journ. Sci.*, vii., 187; Neubauer, *Zeit. Anorg. Chem.*, ii., 45—50; iv., 251—266; x., 60—65; *Zeit. Angew. Chem.*, 1896, 435—440; *Journ. Am. Chem. Soc.*, xvi., 289), on the other hand, tends to pass under the influence of ammonium salt toward the condition of the diammonium magnesium phosphate which yields the metaphosphate on ignition. Further, in the cases of zinc and cadmium (Austin, *Am. Journ. Sci.*, viii., 206) it has been my experience that the presence of a considerable amount of ammonium salt is essential to the precipitation of the ideal double ammonium phosphates of both these elements, although, in the case of cadmium, too large an amount of the ammonium salt prevents complete precipitation and apparently occasions the formation of a phosphate too rich in ammonia. The solvent effect of the reagents in the case of mercury phosphate (Austin, *Am. Journ. Sci.*, viii., 206) is very great, yielding a new salt the composition of which has not been investigated in recent years. Beryllium (Roessler, *Zeit. Anal. Chem.*, xvii., 148) is only partly converted to that ammonium beryllium phosphate which yields the pyrophosphate on ignition, even in the presence of large amounts of ammonia salt. Neither an ammonium salt nor ammonia in solution converts the phosphates of barium, strontium, and calcium (Austin, *Am. Journ. Sci.*, viii., 206) to the double ammonium phosphates. Of these three elements barium alone falls in the form of the hydrogen barium orthophosphate. In certain recent articles upon the precipitation of the double ammonium phosphates some of the facts mentioned above have been called in question.

In the determination of zinc and manganese Dakin (Chemical News, lxxxii., 101; lxxxiii., 37) has proposed to substitute ammonium phosphate as the precipitant in place of microcosmic salt (hydrogen ammonium sodium phosphate) in presence of a considerable amount of ammonium chloride, and to wash with a 1 per cent solution of the precipitant followed by alcohol. Dakin's analytical results, taken without scrutiny, would seem to show that the precipitate produced by ammonium phosphate (in only moderate excess), and washed with a 1 per cent solution of the precipitant and alcohol, has the ideal constitution of the double phosphate and leaves upon ignition the pyrophosphate.

From the standpoint of theory it is difficult to see why the ammonium phosphate should be more effective in producing the normal ammonium double salt than is hydrogen ammonium sodium phosphate in amount sufficient to supply the ammonium equivalent, or than a mixture of the equivalent amount of any soluble phosphate in association with enough ammonium salt to supply the same amount of the ammonium radical or ion. Whether the conversion of the tribasic phosphate of the type $R^{II}_3P_2O_8$ to the double ammonium phosphate of the type $(NH_4)R^{II}PO_4$ be viewed either as dependent upon the interaction according to mass of reagents assembled, or from the point of view of the ion theory (Gooch and Austin, *Am. Journ. Sci.*, vi., 233; Boettger, *Ber. Chem. Gesell.*, xxxiii., 1019), the action of a solution of ammonium phosphate should not differ much from that of equivalent amounts of other ammonium salt and soluble phosphate. My own experience with the double ammonium zinc phosphate confirms this view (*Am. Journ. Sci.*, viii., 210). In the accompanying table are reproduced from my former paper the data of certain experiments bearing upon this point. (See next page).

The results of the experiments of Section B, in which the precipitation was made by microcosmic salt in presence of a small amount of ammonium chloride, show an average constitution of the precipitate similar to that of the precipitate obtained in A by an equivalent amount of ammonium phosphate; but the results of both series, A and B, vary considerably from the ideal much more closely approximated in the experiments of C, in which precipitation was made in the presence of a large excess of ammonium chloride. With these results those of Dakin are not in accord. Upon examination, however, Dakin's procedure appears to be open to criticism.

In the first place, it appears that the asbestos employed by Dakin was of the hydrous (serpentine) variety, which disintegrates when heated and is readily acted on by many reagents. Though previously treated with hydrochloric acid, it was, by Dakin's account, preceptibly soluble in a solution of ammonium phosphate. After

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. xiv., No. 80.

	$Zn_2P_2O_7$ corresponding to $ZnSO_4$. Taken. Grm.	Found. Grm.	Error in terms of $Zn_2P_2O_7$. Grm.	Error in terms of zinc. Grm.	Zinc left in the filtrate.	$(NH_4)_3PO_4$. Grms.	NH_4Cl. Grms.	Time of standing. Hours.
				A.				
1.	0·6355	0·6206	0·0149 −	0·0060 −	Trace	3·13	—	1½
2.	0·6355	0·6254	0·0101 −	0·0040 −	,,	3·13	—	16
3.	0·6355	0·6300	0·0055 −	0·0022 −	,,	3·13	—	16
				B.		$HNaNH_4PO_4.4H_2O$.		
4.	0·6355	0·6271	0·0084 −	0·0034 −	Trace	4·47	0·5	1
5.	0·6355	0·6256	0·0099 −	0·0040 −	None	4·47	0 5	20
				C.				
9.	0·6355	0·6335	0·0020 −	0·0008 −	None	4·47	10	16
10.	0·6355	0 6381	0·0026 +	0·0010 +	,,	4·47	20	½
11.	0·6355	0·6379	0·0024 +	0·0009 +	,,	4·47	20	2
12.	0·6355	0 6386	0·0031 +	0·0012 +	,,	4·47	20	½
13.	0·6355	0·6393	0 0038 +	0·0014 +	,,	4·47	20	½
14.	0·6367	0·6355	0·0012 +	0·0005 +	,,	4·47	30	16

drying at 100°—105° the crucible and felt lost some decimilligrms. on ignition. It was on this account that Dakin weighed precipitate and filter, after drying at 100°—105°, when the double phosphate was to be estimated as such, or after ignition when the zinc pyrophosphate was weighed, and then, dissolving the precipitate in nitric acid, re-weighed the crucible and asbestos, and by difference from the former weight obtained the apparent weight of the precipitate. The inevitable loss through disintegration or solubility of the filter in the nitric acid used to dissolve the precipitate in Dakin's procedure, must raise the corresponding apparent weight of the precipitate itself. Any series of results based upon the use of such material must of necessity be imperfect to the extent to which the ignited filter disintegrates or dissolves under the action of the nitric acid used to dissolve the precipitate.

Anhydrous (amphibole) asbestos, the material of which I made use, is insoluble, under the conditions of analytical work, in ordinary reagents, including even the strong acids, as has been abundantly shown (Gooch, *Am. Chem. Journ.*, i., 317; Mar, *Am. Journ. Sci.*, xii., 288; xliii., 521; Browning, *Am. Journ. Sci.*, xliv., 399; Phinney, *Am. Journ. Sci.*, xlv., 468). It is likewise completely insoluble in ammonium phosphate under the conditions of the work described, as I have found by experiment. Herein lies one cause of difference between Dakin's results and mine.

A second source of error in Dakin's procedure is found in the fact that precipitates of the double ammonium phosphates are washed in a 1 per cent solution of the reagent, ammonium phosphate followed by "re-distilled alcohol." Dakin calls attention to the fact that absolute alcohol must not be used, but makes no mention of the exact strength of the alcohol employed in his work.

In order to test the insolubility of ammonium phosphate in alcoholic washing I have made various experiments, the details of some of which are given in the following account. Portions of a solution of manganous chloride, standardised as the sulphate according to the method (*Am. Journ. Sci.*, v., 209) described in a former paper, were carefully measured from a burette, ammonium chloride and microcosmic salt were added in the proportions formerly recommended, and precipitation of the ammonium manganese phosphate was completed exactly as directed. After cooling, the precipitates were collected on asbestos under pressure in a perforated platinum crucible. In the experiments, the results of which are given under A of the table, the precipitate was in each case washed with distilled water made faintly ammoniacal, while in those recorded under B, C, and D of the table the precipitate was washed with 200 c.c. of a 1 per cent ammonium phosphate solution, and rinsed with 40 c.c. of alcohol of different strengths,—60, 80, and 88 per cent,—applied in successive portions.

	Grm.	Grm.
$Mn_2P_2O_7$ corresponding to $MnCl_2$ taken	0·3020	
A. Washed with ammoniacal water ..	0·3042	0·3020
B. Washed with 1 per cent $H(NH_4)_2PO_4$, rinsed with 60 per cent alcohol ..	0·3050	0·3041
C. Washed with 1 per cent $H(NH_4)_2PO_4$, rinsed with 80 per cent alcohol ..	0·3058	0·3074
D. Washed with 1 per cent $H(NH_4)_4PO_4$, rinsed with 88 per cent alcohol ..	0·3066	0·3086

From these experiments it appears that the procedure involving the washing of a precipitate of ammonium manganese phosphate by a 1 per cent solution of ammonium phosphate, draining with the pump, and then completing the washing with alcohol, results in a contamination of the precipitate proportionate to the strength of the alcohol used. Even the thin felt of asbestos alone when washed with ammonium phosphate followed by alcohol retains amounts of that salt proportionate to the strength of the alcohol employed. This is shown in the accompanying statement.

	Grm.
Weight of asbestos felt	0·0681
Weight of asbestos felt after washing ten times with a 1 per cent solution of ammonium phosphate and rinsing with distilled water	0·0681
Weight of asbestos felt after washing with a 1 per cent solution of ammonium phosphate and rinsing with alcohol of the strength given	0·0682 (60 per cent) 0·0684 (80 ,,) 0·0686 (88 ,,)

So it appears that in washing with ammonium phosphate and alcohol, according to Dakin's procedure, the precipitate of the double ammonium phosphate must be loaded with foreign material to a degree dependent upon the conditions. This error is in the same direction as that introduced by the solubility of the serpentine in nitric acid. With these two sources of error active, the most remarkable thing about Dakin's results is that they happen to agree so closely with mine, the solubility of the serpentine asbestos and the insolubility of the ammonium phosphate in alcohol together counterbalancing the deficiency due to imperfect constitution of the double ammonium phosphate.

As to the experience of Miller and Page (*School of Mines Quarterly*, xxii., 391) upon the ammonium cadmium phosphate, in consequence of which they concluded not only that my method for the estimation of cadmium is unsatisfactory, but that "asbestos filters should be avoided on account of the solvent action of either ammonium phosphate or nitric acid," it is sufficient to direct attention to the fact that their analytical examination of

this process is wholly worthless by reason of their use of serpentine asbestos.

With suitable anhydrous asbestos at disposal, the estimation of magnesium, manganese, cadmium, and zinc precipitated as the double ammonium phosphate, according to the directions, and with the precautions laid down in the former papers from this laboratory to which reference has been made, is perfectly practicable. Concerning the manganese and zinc phosphates, in particular, it may be reiterated that with a sufficiency of ammonium salt, preferably the chloride, and with an excess of the precipitant present, the precipitation is complete, and the phosphate formed of nearly ideal constitution. In the precipitation of the ammonium cadmium phosphate the proportions of the reagents must be regulated with care. The use of ammonium phosphate followed by rinsing in alcohol is not only wholly unnecessary but always altogether undesirable.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, January 21st, 1903.

Prof. J. Emerson Reynolds, Sc.D., F.R.S., President, in the Chair.

Mr. W. H. Edwards was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. George Henry Appleyard, 151, Cleveland Street, Hull; Samuel Bradbury, Thornham New Road, Castleton; George Thomas Branch, Claremont, Cape Town, S. Africa; Hubert William Bywaters, 11, King Street, Regent Street, W.; William Henry Cadman, Lord Williams's Grammar School, Thame; John Castell-Evans, 141, Ferme Park Road, Crouch End, N.; Arthur John Codling, 5, Tavistock Square, W.C.; Benjamin Claxton Coyle, 65, Lansdowne Road, Dublin; Cecil Henry Desch, Instow, Mount Pleasant Road, Tottenham, N.; Leonard King Hindmarsh, 354, Lordship Lane, S E.; Franklin Wise Howorth, Rose Bank, Elmdale Road, Palmer's Green, N.; Arthur Graham Leigh, Chorcliff House, Chorley; Percy George Mander, Spon House, Spon End, Coventry; Frederick O'Brien, 15, Lilymead Avenue, Knowle, Bristol; Alec Bowring Steven, Ness House, Surbiton; George Malcolm Thomson, Newington, Dunedin, N.Z.; Stanley Tolson, 14, Furnivall Road, Balby, Doncaster; Francis Digby Toyne, Santubong, Sarawak; Thomas Crosbie Walsh, "Sunnyside," Muswell Avenue, Muswell Hill, N.; David John Williams, 1, St. Agnes Place, Kennington Park, S.E.

The Secretary announced that a communication had been received from Profs. Börnstein and Meyerhoffer stating that they were engaged in revising the *Physikalisch-chemische Tabellen* of Landolt and Börnstein, and would welcome from English chemists any suggestions of alterations or corrections for the new edition, addressed to them, "care of Verlag von Julius Springer, Berlin, N."

The Council has ordered the following report to be printed in the *Journal* and in the *Proceedings* of the Society:—

Report of the International Committee on Atomic Weights.

In the year 1900, an International Committee on atomic weights was organised, composed of more than fifty representatives from chemical and other societies. Its conferences were necessarily conducted by correspondence, and the delays and difficulties of the work proved to be both serious and annoying. Accordingly, the Committee, by vote, designated a smaller body of three representatives, and the latter now has the honour to report its recommendations.

On the fundamental question of standards, definite and formal action seems to be impracticable. By the original committee of the German Chemical Society, the oxygen standard was adopted, but that proposal, whilst receiving strong support, also met with serious opposition. In fact, opinion as expressed by individual voices seems to be somewhat evenly divided upon this question, and around it there has already grown up a controversial literature of formidable proportions. To force the adoption of either standard, oxygen or hydrogen, appears therefore to be impossible, and for some time to come both are likely to be employed. Between them, experience must be the final arbiter. That standard which best serves to co-ordinate chemical and physical knowledge will ultimately be chosen, and the other will gradually fall into disuse. Meanwhile, it is important that the most probable values for the several atomic weights should be indicated, and that every table of them should be consistent within itself. Such a table has been prepared by our distinguished predecessors, and its revision, as knowledge advances, seems to be our proper function.

In order that our work may be of the most general service, we have prepared a table in which both standards of atomic weight are represented. In most of its details it is identical with the table which was reported by the previous committee at the beginning of the year 1902 (in No. 1 of the *Berichte* for 1902). Some changes, however, have, in our judgment, become necessary, and these may be briefly indicated as follows:—

Antimony.—In the former reports of the commitee, the value derived by Cooke from analyses of the bromide, Sb = 120, was adopted. This, however, ignores the work of Cooke and of Schneider upon antimony trisulphide, and the still more recent determinations made by Friend and Smith. The true number being therefore in doubt, we recommend the use of an average value, and put Sb = 120·2 (O = 16).

Germanium.—The number 72·5 is more nearly in accord with Winkler's determinations than the former number 72.

Hydrogen.—In the column which represents the oxygen standard, hydrogen has heretofore been assigned the value 1·01. The number 1·008 is, however, much more exact, and the error in 1·01 is too large to be perpetuated. Each figure should be given to the nearest *significant* decimal.

Lanthanum.—During 1902, two new determinations of the atomic weight of lanthanum were published. According to Jones, La = 138·77. Brauner and Pavlícek found La = 139·04. Both investigations were conducted with great skill and care, and each one seems to have some points of advantage over the other. The average, La = 138 9, appears to be the safest value to adopt. These data naturally influence our judgment in the case of cerium, and we retain Brauner's number, Ce = 140, rather than adopt the lower estimates made by other observers.

Mercury.—Taking into account all the determinations which have appeared, and giving great weight to the most recent measurements by Hardin, we regard the value Hg = 200 as best warranted by the existing evidence.

Palladium.—The atomic weight of this metal is in doubt. The best determinations give values ranging from 106 to 107. The mean between them, Pd = 106·5, has been provisionally adopted.

Radium.—This element appears in the table for the first time. Madame Curie's determination of the atomic weight, Ra = 225, is probably not far from the truth.

Selenium.—Judging from the work of Lenher, and the very recent determinations by Jul. Meyer, the former value, Se = 79·1, is probably too low. In order to give due weight to the newer measurements, we write Se = 79·2.

Tin.—The determinations by Bongartz and Classen, which seem to be the best, make Sn = 119. The former value, 118·5, is almost certainly too low.

Uranium.—According to the very recent investigation

by Richards and Merigold, the atomic weight of uranium is 238·5.

Zirconium.—The figure Zr=90·6 is apparently the most probable.

In thus assuming the duties assigned to us by the larger International Committee, we act upon the conviction that the purpose of our appointment is to secure the promptness and efficiency which is only possible with a comparatively small working body. In order to carry out this purpose, we must depend upon the co-operation and assistance of our colleagues. We therefore beg that they, and also all other chemists who are interested in researches upon atomic weights, will aid us with their criticisms and advice. We especially ask that publications upon the subject shall be sent to us, in triplicate if possible, so that no matter of importance may be overlooked. Without support of this kind our work cannot be made fully effective.

The complete table of atomic weights, with foregoing changes incorporated, follows.

F. W. Clarke
T. E. Thorpe } *Committee.*
Karl Seubert

International Atomic Weights. (1903).

		O=16.	H=1.
Aluminium	Al	27·1	26·9
Antimony	Sb	120·2	119·3
Argon	A	39·9	39·6
Arsenic	As	75·0	74·4
Barium	Ba	137·4	136·4
Bismuth	Bi	208·5	206·9
Boron	B	11	10·9
Bromine	Br	79·96	79·36
Cadmium	Cd	112·4	111·6
Cæsium	Cs	133	132
Calcium	Ca	40·1	39·8
Carbon	C	12·00	11·91
Cerium	Ce	140	139
Chlorine	Cl	35·45	35·18
Chromium	Cr	52·1	51·7
Cobalt	Co	59·0	58·56
Columbium (Niobium)	Cb	94	93·3
Copper	Cu	63·6	63·1
Erbium	E	166	164·8
Fluorine	F	19	18·9
Gadolinium	Gd	156	155
Gallium	Ga	70	69·5
Germanium	Ge	72·5	71·9
Glucinum (Beryllium)	Gl	9·1	9·03
Gold	Au	197·2	195·7
Helium	He	4	4
Hydrogen	H	1·008	1·000
Indium	In	114	113·1
Iodine	I	126·85	125·90
Iridium	Ir	193·0	191·5
Iron	Fe	55·9	55·5
Krypton	Kr	81·8	81·2
Lanthanum	La	138·9	137·9
Lead	Pb	206·9	205·35
Lithium	Li	7·03	6·98
Magnesium	Mg	24·36	24·18
Manganese	Mn	55·0	54·6
Mercury	Hg	200·0	198·5
Molybdenum	Mo	96·0	95·3
Neodymium	Nd	143·6	142·5
Neon	Ne	20	19·9
Nickel	Ni	58·7	58·3
Nitrogen	N	14·04	13·93
Osmium	Os	191	189·6
Oxygen	O	16·00	15·88
Palladium	Pd	106·5	105·7
Phosphorus	P	31·0	30·77
Platinum	Pt	194·8	193·3
Potassium	K	39·15	38·86
Praseodymium	Pr	140·5	139·4
Radium	Ra	225	223·3
Rhodium	Rh	103·0	102·2
Rubidium	Rb	85·4	84·8
Ruthenium	Ru	101·7	101·0
Samarium	Sm	150	148·9
Scandium	Sc	44·1	43·8
Selenium	Se	79·2	78·6
Silicon	Si	28·4	28·2
Silver	Ag	107·93	107·12
Sodium	Na	23·05	22·88
Strontium	Sr	87·6	86·94
Sulphur	S	32·06	31·83
Tantalum	Ta	183	181·6
Tellurium	Te	127·6	126·6
Terbium	Tb	160	158·8
Thallium	Tl	204·1	202·6
Thorium	Th	232·5	230·8
Thulium	Tm	171	169·7
Tin	Sn	119·0	118·1
Titanium	Ti	48·1	47·7
Tungsten	W	184·0	182·6
Uranium	U	238·5	236·7
Vanadium	V	51·2	50·8
Xenon	X	128	127
Ytterbium	Yb	173·0	171·7
Yttrium	Yt	89·0	88·3
Zinc	Zn	65·4	64·9
Zirconium	Zr	90·6	89·9

Of the following papers, those marked * were read:—

*1. "*Researches on Silicon Compounds.* Part VIII. *Interactions of Silicophenylamide with Thiocarbimide.*" By J. Emerson Reynolds.

The author has shown that the fine, crystalline silicophenylamide, $Si(NHC_6H_5)_4$, described in Part V. of this series of papers, loses aniline on careful heating, and affords, first, silicotriphenylguanidine and, subsequently, silicodiphenylimide (*Trans.*, 1900, lxxvii., 836).

The comparative ease and completeness with which the change $Si(NHPh)_4 = Si(NPh)_2 + 2NH_2Ph$ can be realised suggested another mode of producing the di-mide, involving the action of thiocarbimides. It was anticipated that silicophenylamide would react in the following manner: $Si(NHPh)_4 + 2R'N:CS = Si(NPh)_2 + 2CSN_2H_2PhR'$.

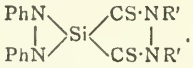
Whilst the above change can be realised, the author showed that the marked tendency of silicon to form complex molecules lead to other and unexpected interactions with thiocarbimides, and found that:—

1. Silicophenylamide in benzene solution is not decomposed by a thiocarbimide, even at the boiling-point of the solvent, but addition compounds are formed. For example, ethyl thiocarbimide in excess gives fine needle-like crystals consisting of $Si(NHPh)_4,2EtNCS$, and, when not in excess, rhombic plates of $Si(NHPh)_4,EtNCS$. Both compounds lose the whole of the thiocarbimide at 100°, and leave silicophenylamide unchanged.

2. A very different result is obtained when one molecule of silicophenylamide and two molecules of a thiocarbimide, without a solvent, are heated in sealed tubes at 160°. At first, the two compounds unite directly as before, but when the temperature rises to 140° a thick, slightly brown liquid begins to form, the production of which is complete on heating to 160° for half an hour. At the ordinary temperature, this substance is a very viscid liquid, and a specimen of the ethyl compound has been kept for several months without separation of any crystals. Methyl, ethyl, and phenyl thiocarbimides afford similar products, which have no odour of thiocarbimide, even when strongly heated; they are easily miscible with benzene, from which they are precipitated on addition of ligroin, and may thus be purified by a repetition of this treatment. Prolonged digestion of the benzene solution of each substance leads to a slow separation of silicodiphenylimide, whilst the liquid affords crystals of a di-substituted thiocarbamide. Therefore the interaction

anticipated actually does take place at a sufficiently high temperature, but the resulting silicon di-imide and thiocarbamide unite to form a homogeneous liquid consisting of $Si(NPh)_2,2CSN_2H_2PhR'$, which is slowly dissociated in boiling benzene.

3. Silicophenylamide also interacts with 4 molecules of thiocarbimides at 160°, but not with more than 4 molecules. The products are also viscid liquids at first, but they are not homogeneous, as crystals form to a relatively small extent in the mass on standing for some time, and are those of a substituted thiocarbamide. The liquid portion consists, in each case, of a new substance resulting from the action of the two additional molecules of thiocarbimide on the silicon di-imide produced in the first interaction. These liquids are miscible with benzene, but do not dissociate in it; they are decomposed by alcohol, and afford ethyl orthosilicate, alkyl dithiocarbamate, and a guanidine derivative, hence their constitution is probably—



Silicodiphenylimide, produced by heat from silicophenylamide, combines directly with thiocarbimides to form compounds of this type.

*2. "*On the Relation between the Absorption Spectra and the Chemical Structure of Corydaline, Berberine, and other Alkaloids.*" By J. J. Dobbie and A. Lauder.

It has been proved by purely chemical investigations that corydaline and berberine are closely related to one another, and that both alkaloids are constructed on the same general plan as papaverine, narcotine, hydrastine, and narceine.

An examination of the absorption spectra of the members of this group of alkaloids shows that those which are most closely related structurally give similar spectra, the differences in the spectra becoming more pronounced as the structural differences increase in importance. Thus corydaline and tetrahydroberberine closely resemble each other in structure, and the spectra of the latter only differ from those of the former in the somewhat greater general absorption which they exhibit. Narcotine only differs from hydrastine in containing an additional methoxyl group, and their spectra are almost identical, but quite distinct from those of corydaline, from which both differ considerably in structure. Papaverine and narceine are constitutionally still further removed from corydaline, and their spectra show a correspondingly increased difference as compared with those of the other members of the group. When papaverine, however, is reduced to tetrahydropapaverine, its constitution then corresponds much more closely with that of corydaline, and the spectra of the reduced compound are similar to those of corydaline.

When the corresponding derivatives of corydaline and tetrahydroberberine are compared, it is seen that the latter only differ from the former in possessing a slightly greater absorptive power. Since the only structural difference between the two series of derivatives consists in the replacement of two of the methoxyl radicles of corydaline by the dioxymethylene group in berberine, it was inferred that the difference in the amount of general absorption must be due to this difference of structure, and that the dioxymethylene complex must consequently exert a more powerful absorption than two methoxyl groups. The correctness of this inference received support from the direct comparison of the spectra of piperonylic acid, $C_6H_3(O_2CH_2)CO_2H$, with those of veratric acid, $C_6H_3(OMe)_2{\cdot}CO_2H$.

Whilst the spectra of ω-aminoethylpiperonylcarboxylic anhydride, $C_9H_7NO(O_2CH_2)$, from berberine, and of corydaline, $C_9H_7NO(OMe)_2$, from corydaline are very similar, they differ widely from those of cotarnine and hydrastinine, the corresponding oxidation products of narcotine and hydrastine respectively. This difference finds a sufficient explanation in the fact that the pyridine ring, which is closed in corydaline and ω-aminoethylpiperonylcarboxylic anhydride, is open in cotarnine and hydrastinine. The action of potassium hydroxide converts hydrastinine into oxyhydrastinine, in which the pyridine ring is closed. The spectra of oxyhydrastinine and corydaline are almost identical.

Hartley (*Phil. Trans.*, 1885, Part II., 471) has already shown that many of the alkaloids give highly characteristic spectra, and has pointed out the applicability of the method to the study of their constitution. The authors draw certain general conclusions as to the relation between the structure and the absorption spectra of the alkaloids. These conclusions are based chiefly on the results of the examination of the alkaloids of the corydaline group, but are supported by the results of the examination of other alkaloids.

Alkaloids which differ essentially in structure, even when their molecular formulæ are the same, give dissimilar spectra, whilst alkaloids which are closely related structurally give similar spectra, and sometimes, when the structural resemblance is very close, spectra which are indistinguishable from one another,

Stereoisomeric alkaloids give identical spectra. In the examination of stereoisomeric phenomena, the spectroscope affords a means of determining whether two substances of the same formula, the one active and the other inactive, are related to one another as stereoisomerides. If they give different spectra, it can be inferred with great certainty that they differ structurally.

Homologous alkaloids give practically the same spectra. The formula of bulbocapnine differs from that of tetrahydroberberine and papaverine only by CH_2, but the wide difference between the spectra of all three substances precludes the possibility that bulbocapnine is homologously related to either. Whilst important differences of structure are always accompanied by marked differences in the spectra, many of the structural details of an alkaloid may be modified without any appreciable effect being produced in the spectra. An example of this is afforded by the replacement of two of the methoxyl groups of corydaline by the dioxymethylene group in berberine. When, therefore, two alkaloids give spectra which are nearly, but not quite, identical, it may be inferred with considerable probability that they differ only in minor details of structure. In such cases, a preliminary spectroscopic examination would sometimes give a clue to the constitution of an alkaloid which would greatly facilitate the chemical investigation.

*3. "*The Absorption Spectra of Laudanine and Laudanosine in relation to their Chemical Constitution.*" By J. J. Dobbie and A. Lauder.

In this paper, the absorption spectra of laudanine, $C_{20}H_{25}O_4N$, and laudanosine, $C_{21}H_{27}O_4N$, two rare opium alkaloids discovered by Hesse, are described. They are shown to be practically identical with one another, and, further, to resemble very closely the spectra of corydaline and tetrahydropapaverine (see preceding abstract). The close resemblance between the spectra of laudanine and laudanosine confirms the view that they are homologous bodies, whilst the close agreement with the spectra of corydaline and tetrahydropapaverine points to the possession of a structure similar to that of these alkaloids.

For reasons given below, the relationship with corydaline is probably somewhat closer than with tetrahydropapaverine. Laudanosine has one atom of carbon less than corydaline, the number of hydrogen, oxygen, and nitrogen atoms being the same in both. Assuming the formulæ of the two alkaloids to have been correctly determined, the difference between them may conceivably consist in the absence from laudanosine of the methyl group which is present in corydaline and in the partial reduction of one of its rings,—

$$\underset{\text{Corydaline.}}{C_{22}H_{27}O_4N} - CH_2 + H_2 = \underset{\text{Laudanosine.}}{C_{21}H_{27}O_4N}.$$

In this way, the close agreement of the spectra might be accounted for. The absence of the methyl group would produce no appreciable effect, and it is known from the examination of a number of cases that the introduction of two atoms of hydrogen into a molecule is not necessarily accompanied by any notable modification of its spectra. The spectroscopic evidence as to the close relationship subsisting between laudanosine and corydaline is substantiated by the little which is known concerning the chemistry of the former alkaloid. Like corydaline, it contains four methoxyl groups, and yields metahemipinic acid as one of its oxidation products. It further resembles corydaline in the ease with which it is oxidised by nitric acid to a yellow base. This basic product has not been analysed, but it is not improbably identical with meconidine, an alkaloid associated with laudanosine in opium. The formula of meconidine is $C_{21}H_{23}O_4N$, and bears the same relationship to that of laudanosine that the formulæ of dehydrocorydaline and berberine respectively bear to those of corydaline and tetrahydroberberine.

Colourless :—

Corydaline.	Tetrahydroberberine.	Laudanosine.
$C_{22}H_{27}O_4N$.	$C_{20}H_{21}O_4N$.	$C_{21}H_{27}O_4N$.
M. p. 135·5°.	M. p. 167°.	M. p. 89°.

Yellow :—

Dehydrocorydaline.	Berberine.	Meconidine.
$C_{22}H_{23}O_4N$.	$C_{20}H_{17}O_4N$.	$C_{21}H_{23}O_4N$.
M. p. 118—120°.	M. p. 145°.	M. p. 58°.

Whether the yellow substance produced by the oxidation of laudanosine is identical with meconidine or not, the mere fact of the existence in opium of the coloured base having a formula differing from that of laudanosine by four atoms of hydrogen affords support to this view of the relationship of these substances, and this hypothesis receives additional confirmation from a comparison of the melting-points of the substances.

Discussion.

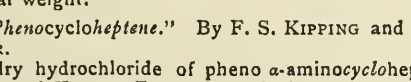
Dr. JOWETT asked if the authors had tried the method with stereoismeric alkaloids like atropine and hyoscyamine or the scopolamines, or whether the method had been confined to those alkaloids with a quinoline or *iso*-quinoline nucleus. If the method was of general application, it would prove of great service in distinguishing between stereoisomerides and isomeric alkaloids differing structurally.

Professor DUNSTAN remarked that Dr. Dobbie had made a distinct step in advance in the direction of showing how these absorption spectra, for a knowledge of which chemists owe so much to Professor Hartley, may be definitely utilised as a criterion in determining the general molecular structure of alkaloids. Though possibly of limited application, the method promised to be of value in dealing with cases, such as those now brought forward by Professor Dobbie, where chemical methods were not yet available or applicable.

Professor DOBBIE, in reply, said that although he and Mr. Lauder had incidentally examined some of the pyridine alkaloids, they had not made any systematic study of them, as they had of the alkaloids of high molecular weight.

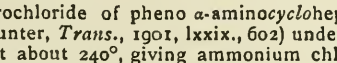
4. "*Phenocycloheptene.*" By F. S. KIPPING and A. E. HUNTER.

The dry hydrochloride of pheno α-amino*cyclo*heptane (Kipping and Hunter, *Trans.*, 1901, lxxix., 602) undergoes decomposition at about 240°, giving ammonium chloride and phenocy*clo*heptene, a homologue of indene and of dihydronaphthalene :—



Phenocy*clo*pentene. (Indene).

Phenocy*clo*hexene. (Dihydronaphthalene).



Phenocy*clo*heptene.

*Phenocyclo**heptene***, $C_{11}H_{12}$, a colourless liquid having an odour which recalls that of indene, boils at 233·5—234° (757 m.m.), and has a sp. gr. 1·009 at 4°/4°. It differs from indene in chemical properties, as it neither gives a picrate nor a condensation product with benzaldehyde in presence of sodium ethoxide.

On oxidation with potassium permanganate in alkaline solution at the ordinary temperature, phenocy*clo*heptene is converted into an acid identical with the phenylbutyric-*o*-carboxylic acid, $CO_2H{\cdot}C_6H_4{\cdot}[CH_2]_3{\cdot}CO_2H$, prepared synthetically by Roser (*Ber.*, 1885, xviii., 3118); this acid seems to be dimorphous, as, when first produced, it crystallises in needles melting at 122°, and subsequently in plates melting at 138°, the latter being the form obtained by Roser, but the conditions which determine the formation of the one or other modification could not be ascertained. On oxidation with hot, very dilute nitric acid, the unsaturated hydrocarbon gives the form melting at 138°.

5. "*The Influence of Molybdenum and Tungsten Trioxides on the Specific Rotations of* l-*Lactic Acid and Potassium* l-*Lactate.*" By G. G. HENDERSON and J. PRENTICE.

Both molybdenum trioxide and tungsten trioxide are dissolved by a hot aqueous solution of potassium *l*-lactate, the former readily, but the latter with greater difficulty. In each case, the specific rotation increases with the quantity of oxide in solution, and reaches a maximum ($[\alpha]_D$ 20° = +22·69° and +10·8° respectively) when the substances are present in the proportion of 2 molecules of $C_3H_5O_3K$ to 1 molecule of RO_3. At this point, the solutions are practically saturated with the oxides, for, although a little more of each oxide can be dissolved in the heat, decomposition then ensues, and the solutions become coloured blue or brown according as molybdenum or tungsten trioxide is used. These results point to the formation of potassium molybdilactate and tungstilactate according to the equation :—

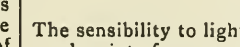
$$2C_3H_5O_3K + RO_3 = RO_2(C_3H_4O_3K)_2 + H_2O.$$

Sodium molybdate and tungstate are readily dissolved by an aqueous solution of *l*-lactic acid, the specific rotation increasing in each case as larger quantities of the salt are added. The highest readings ($[\alpha]_D$ 20° = +21·15° and +9·9°) are obtained when the solutions contain 1 molecule of Na_2RO_4 for each 2 molecules of $C_3H_6O_3$, and if a larger quantity of either salt is added the rotation diminishes. It seems, therefore, that a reaction occurs in the sense of the equation—

$$2C_3H_6O_3 + Na_2RO_4 = RO_2(C_3H_4O_3Na)_2 + 2H_2O,$$

sodium molybdilactate and tungstilactate being formed.

Molybdenum trioxide is also dissolved by an aqueous solution of *l*-lactic acid, but the compound formed in the solution is decomposed by exposure to heat or even to diffused daylight, and hence the process of dissolution must be carried on in the cold and in a dark place. The specific rotation increases as the oxide is added, and reaches a maximum ($[\alpha]_D$ 20° = +24·78°) when 1 molecule of MoO_3 is present for each 1 molecule of $C_3H_6O_3$, diminishing again on the addition of more oxide. This result indicates the formation of a compound $CHMe(CO_2H)O{\cdot}MoO_2{\cdot}OH$, or more probably—



The sensibility to light of the solution is so great that a good print from a negative can be taken on paper saturated with the solution and dried in the dark, but the blue colour of the print fades away in the absence of light.

Tungsten trioxide was found to be practically insoluble in an aqueous solution of *l*-lactic acid.

According to the views formerly expressed (*Trans.*, 1899, lxxv., 542) regarding the constitution of the "tartar emetic" class of compounds, molybdenum and tungsten

trioxides should react with lactates, yielding derivatives of the type $RO_2(O{\cdot}CHMe{\cdot}CO_2M)_2$, and the results of this investigation point to the formation of compounds having this composition.

6. "*Estimation of Ethyl Alcohol in Essences and Medicinal Preparations.*" By T. E. THORPE and JOHN HOLMES.

The authors described a method of estimating ordinary alcohol in essences and medicinal preparations containing essential oils and volatile substances, such as ether, chloroform, benzaldehyde, camphor, compound ethers, and which has been used for some time past in the Government Laboratory, and which has been found to be both accurare and of very general applicability.

It is as follows:—Twenty-five c.c. of the sample, measured at 15·5°, are mixed with water in a separator to a bulk of from 100 to 150 c.c., and common salt is added in sufficient quantity to saturate the liquid. The mixture is now shaken vigorously for five minutes with from 50 to 80 c.c. of light petroleum boiling below 60°, and after standing for about half-an-hour the lower layer is drawn off into another separator, extracted, if necessary, a second time with petroleum, and then introduced into a distillation flask. Meanwhile, the petroleum layers are washed successively with 25 c.c. of saturated brine, the washings added to the main bulk, which is neutralised if necessary, and then distilled, and the distillate made up to 100 c.c. and its relative density determined at the standard temperature in the usual manner. The results thus obtained require a small correction from the circumstance that, as the alcohol present is distilled into four times its initial volume, the errors of the spirit tables are necessarily quadrupled. Details were given of the mode in which the magnitude of this error may be determined, and from these results the mean error of the tables at below 40 per cent proof (for example, 0·972 sp. gr.), which is the particular section of tables mainly used, may be set down as +0·2 per cent of proof spirit, and hence the observed determinations, expressed as percentages of proof spirit, require a subtractive correction of 0·8 per cent.

Tables were given of results obtained on preparations actually made in the laboratory and containing known quantities of ethyl alcohol, as evidence of the accuracy and general applicability of the method and of the degree of variation which may be expected to occur between the results of different operators.

7. "*Carbon Monoxide as a Product of Combustion of the Bunsen Burner.*" By T. E. THORPE.

The author, in the course of an inquiry into the nature of the combustion-products of certain of the gas- and oil-stoves in common use, has had occasion to make observations on the behaviour of the Bunsen burner as regards its liability to evolve carbon monoxide when burning under an ordinary laboratory sand-tray. He finds that a burner fed with coal-gas at the rate of 6 cubic feet per hour, and under 0·95 inch pressure, will evolve about 0·022 cubic foot of carbon monoxide when burnt under a sand-tray in such manner that the inner cone of the flame impinges, or apparently impinges, on the metal.

8. "*Derivatives of β-Resorcylic Acid and of Protocatechuic Acid.*" By W. H. PERKIN, junr., and E. SCHIESS.

The authors have been engaged for some time in the investigation of some derivatives of these acids, and the appearance of a paper by Bülow and Reiss (*Ber.*, 1902, xxxv., 3900), which deals with somewhat similar derivatives obtained from α-resorcylic acid, has necessitated the publication of the following short account of their results:—

Methyl dimethyl-β resorcylate, $(OMe)_2C_6H_3{\cdot}CO_2Me$, is readily obtained as a colourless oil boiling at 160—162° under 13 m.m. pressure when β-resorcylic acid is treated with potassium hydroxide and methyl sulphate in aqueous solution. The corresponding ethyl dimethyl-β-resorcylate boils at 170° under 13 m.m. pressure.

2 : 4-*Dimethoxybenzoylacetophenone*,—

$$(OMe)_2C_6H_3{\cdot}CO{\cdot}CH_2{\cdot}COPh,$$

is produced when sodium acts on a mixture of ethyl dimethylresorcylate and acetophenone dissolved in dry ether; it crystallises in plates, melts at 55°, and develops a brownish-red colouration with alcoholic ferric chloride. The ethereal solution gives, with copper acetate, the copper compound $C_{34}H_{30}O_8Cu$, which crystallises from benzene in slender, green needles containing 1 molecule of benzene.

2 : 4-*Dimethoxycinnamic acid*,—

$$(OMe)_2C_6H_3{\cdot}CH{:}CH{\cdot}CO_2H,$$

which has already been obtained from methylumbelliferone by Will and Tiemann (*Ber.*, 1882, xv., 2080; 1883, xvi., 2116) in two modifications (α- and β-) melting respectively at 138° and 184°, may be easily prepared synthetically by digesting dimethylresorcylaldehyde (2 : 4-dimethoxybenzaldehyde), $(OMe)_2C_6H_3{\cdot}CHO$, with sodium acetate and acetic anhydride in the usual manner. The acid obtained in this way by the authors was the β-modification melting at 184°.

The *ethyl* salt, $(OMe)_2C_6H_3{\cdot}CH{:}CH{\cdot}CO_2Et$, is very conveniently prepared, in a yield of 80 per cent, by treating a mixture of dimethylresorcylaldehyde and ethyl acetate with sodium (compare Claisen, *Ber.*, 1890, xxiii., 977); it is a colourless oil distilling at 208° under 13 m.m. pressure.

3 : 4-*Dimethoxycinnamic acid* may be obtained by treating dimethylcatecholaldehyde (3 : 4-dimethoxybenz aldehyde) in a similar manner; it crystallises from acetic acid in needles, melts at 180°, and is identical with the acid which Tiemann and Will (*Ber.*, 1881, xiv., 960) first prepared from caffeic and ferulic acids by treatment with potassium hydroxide and methyl iodide. Its *ethyl* salt may be prepared from the acid by esterification in the usual manner, but much more conveniently by acting on a mixture of dimethylcatecholaldehyde and ethyl acetate with sodium. It crystallises from light petroleum in plates, melts at 59°, and distils at 196—197° under a pressure of 11 m.m.

Ethyl 3 : 4-*dimethoxyphenyl* α : β-*dibromopropionate*, $(OMe)_2C_6H_3{\cdot}CHBr{\cdot}CHBr{\cdot}CO_2Et$, which is formed when the last-mentioned ethyl salt is treated with bromine in chloroform solution, melts at 111°, and, when hydrolysed with excess of alcoholic potash, is converted into 3 : 4-*dimethoxyphenylpropiolic acid*, $(OMe)_2C_6H_3{\cdot}C{:}C{\cdot}CO_2H$, a colourless, crystalline substance melting at 149°. A detailed investigation of the above substances and their derivatives is in progress.

(To be continued).

The Solvent and Dissociating Properties of Liquid Cyanogen and of Liquid Hydrocyanic Acid.—M. Centnerszwer.—By means of experiments with a large number of mineral and organic substances, the author has confirmed the fact, already established by Gore in 1872, that liquid cyanogen is only a mediocre solvent, and that most bodies are insoluble therein. Correlatively with this fact he has found a very low value for the electric conductivity of liquid cyanogen; it is less than $0{\cdot}7 \times 10^{-6}$. This conductivity is not increased by the addition of salts. If we accept the hypothesis put forward in 1897 by Dutoit and Aston (*Comptes Rendus*, vol. cxxv., p. 240), it results from these facts that the molecule of liquid cyanogen should not be represented by the formula C_2N_2, like gaseous cyanogen, but by the formula CN, or a similar formula. On the other hand, liquid hydrocyanic acid is a good solvent for many substances, and its electric conductivity is much greater, $0{\cdot}496 \times 10^{-6}$. Hydrocyanic solutions of iodide of potassium and of iodide of trimethylsulphine are, on an average, four times better conductors than the corresponding aqueous solutions at a similar concentration and at the same temperature.—*Zeit. Physik. Ch.*, vol. xxxix., p. 217.

NOTICES OF BOOKS.

Theoretical Organic Chemistry. By Julius B. Cohen, Ph.D. London: Macmillan and Co., Ltd. 1902.

The chief difference between this book and the host of other text-books of organic chemistry of about the same scope and difficulty is the large importance attached in it to the consideration of industrial processes and products, which will make it specially useful to teachers and students in technical schools and colleges. Details for performing a great number of experiments are interspersed in the text, though the title gives no suggestion of this feature; these seem to be carefully described and well chosen, and will probably be found sufficient to form an elementary laboratory course in organic chemistry. The general style in which the book is written recalls the descriptive class of text-book, which is apparently now rapidly becoming obsolete and is giving way before those which advocate the research method of studying chemistry. At the end of each chapter there is a collection of questions of the familiar type on the matter contained in it; many of these questions are drawn from University B.Sc. pass-papers, and from the papers of the Board of Education. The book appears to be generally very trustworthy in matters of detail, though the percentage composition of butter given on page 164 cannot be regarded as representing the average, and should be corrected in a future edition. Though no doubt the book will be found useful in preparation for examinations, it would probably be better employed as a book of reference for teachers, than as one to be put into the hands of the students themselves, except in so far as the practical portions, which are very good, are concerned.

Handbuch der Elektrochemie. Specielle Elektrochemie. Lieferung I. ("Manual of Electro-chemistry." Special Electro-chemistry. Part I.). By Dr. H. Danneel. Halle, A.-S.: Wilhelm Knapp. 1903.

With the publication of this volume begins a new manual of electrochemistry which is to give a complete account of all that has hitherto been done in this region. The work is to be issued at intervals in 175 parts, and it is anticipated that it will be finished in about two years. The divisions of the subject are classed under nine headings, which are to be undertaken by eight distinguished collaborators, and every effort will be made to ensure the adequate treatment of every branch. This volume is the first number of the Special Electro chemistry of the elements and their inorganic compounds, and contains details of the preparation of hydrogen and its compounds with oxygen, the halogens and sulphur, also sulphuric and nitric acids, the results of the electrolysis of these compounds being also described. A large portion of the volume is occupied by the consideration of methods of electrolysis of water and its purification by electrical means. If the same standard of excellence is maintained throughout as is reached in this volume, the Handbuch should prove most acceptable to all who are interested in this branch of chemistry.

Beiträge zur Chemischen Physiologie und Pathologie ("Contributions to Chemical Physiology and Pathology"). Edited by Franz Hofmeister. Band III. Heft 7 and 8. Braunschweig: Friedrich Viewig und Sohn. 1902.

This number of the *Beiträge* contains an important paper by Waldemar Stade describing his researches on the ferment, capable of decomposing fats, which exists in the stomach. These researches were undertaken at the instigation of Volhard, who combats the view that this decomposition is due to the action of putrefactive organisms; the author of the paper examines the conditions of action of the supposed unorganised ferment of the gastric juice, and confirms Schütz and Borissow's law connecting the amount of the products of digestion and the square root of the quantity of ferment present. He also formulates a further relation involving the time of action of the ferment. This new law is identical with that discovered by Huppert and Schütz in the course of their recent investigations on the quantitative proportions which obtain in the case of pepsin digestion.

The number also contains amongst others an interesting article on the behaviour of substituted toluenes and amidobenzoic acids in the organism, and a short paper dealing with the determination of hippuric acid, when present only in minute quantities, when Bunge and Schmiedeberg's method does not give good results.

Einführung in die Elektrochemie. ("Introduction to Electrochemistry"). By Peter Gerdes. Halle, A.-S.: Wilhelm Knapp. 1902.

This book is an elementary introduction to electrochemistry, and aims at preparing the student for the task of grappling with more advanced works.

The treatment of the subject is based upon the theory of ionic dissociation, and only the most important electrical laws and theories are considered. The elements of electricity and magnetism are briefly dealt with, chiefly from a practical point of view, and occupy a greater portion of the book than that devoted to the consideration of electro-chemistry proper. At the commencement the book appears to be of a most elementary nature, the simplest language being used in description, but this character is not kept up throughout the volume, which is thus very uneven as regards difficulty; for instance, the wording of the chapter on osmosis and osmotic pressure is not as clear as it might be, and a few diagrams would do much towards rendering the explanations more easily understood. The beginner would also certainly require a good deal of help in the manipulation of some of the experiments to be performed, and at times considerable additional verbal instruction.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwi expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 3, January 19, 1903.

Researches on the Alkaloids of Quinquinas: Quinine and Quinidine. — MM. Berthelot and Gaudechon.—The authors undertake a thermo-chemical investigation of the principal alkalis of quinquinas:—Quinine, quinidine, cinchonine, cinchonidine, and cinchonamine. The composition of all the substances used in this research has been carefully verified by complete analysis. The authors determine first the heat of combustion of the alkalis and their formation from their elements, then the heat of formation of their salts in the solid state, both anhydrous and hydrated, and in solution. These observations throw a new light on the constitution of the natural polyamines of the quinine order, compounds analogous to the ethylenediamines, and on the various degrees of their neutralisation by alkalis. They also throw light on the molecular changes of composition of organic bases from the first moment of their precipitation —changes which are comparable in a certain degree to those of precipitated metallic oxides. The isomerism between the organic alkaloids, such as quinine, compared with quinidine and cinchonine compared with cinchonidine, has been an object of special study; also a comparison between similar groups of alkalis whose composition is different.

Method of Formation of Phenols.—F. Bodroux.—When an organo-magnesium compound is left exposed to

the air it rapidly undergoes decomposition. The water-vapour in the atmosphere decomposes it, liberating hydrocarbon, and at the same time the oxygen of the air acts in the following way:—$\overset{R}{Br}>Mg+O=\overset{R-O}{Br}>Mg$. An excellent example of this reaction is when phenyl-magnesium bromide is treated in the above manner. At the end of a few hours a strong odour of phenol is observed. The compounds thus formed are destroyed by the hydrochloric acid, and an alcohol or phenol is liberated:—$R-\overset{O}{Br}>Mg + HCl = \overset{Cl}{Br}>Mg + R—OH$. The author studies these reactions for various other organo-metallic compounds.

Ethyl Dinitroacetate.—L. Bouveault and A. Wahl.—In a previous paper the authors described the preparation of ethyl nitroacetate by the decomposition of α-ethyl nitrodimethylacrylate under the influence of gaseous ammonia. This method, although giving very good results, necessitates a long series of manipulations. They have therefore devised a method of preparing nitroacetic ether in an easier manner.

MISCELLANEOUS.

Society of Electro-Chemists and Metallurgists.—The new Society of Electro-Chemists was successfully inaugurated last Wednesday at the General Meeting held at St. Ermin's Hotel. After a few introductory remarks had been made by Mr. James Swinburne, Pres.Inst.E.E., the formal motion that the Society be formed was moved by Mr. Joseph Swan, F.R.S., and seconded by Mr. Alexander Siemens. It was stated that similar organisations for the promotion of electro-chemical science and practice had been in existence for a considerable time both in Germany and the United States. The seriousness of adding to the already very great number of existing scientific societies had been keenly felt by the provisional Committee, but up to the present, at any rate, owing to the peculiar nature of the sciences of electro-chemistry and electro-metallurgy, no satisfactory *modus vivendi* had been arrived at for affiliation with an existing organisation. The following Council was unanimously elected:—President—J. W. Swan, F.R.S. Vice-Presidents—Prof. A. Crum-Browne, M.D., D.Sc., F.R.S.; Lord Kelvin, G.C.V.O., F.R.S.; Sir Oliver T. Lodge, D.Sc., F.R.S.; Ludwig Mond, Ph.D., F.R.S.; Lord Rayleigh, D.C.L., F.R.S.; Alexander Siemens, M.Inst.C.E.; J. Swinburne, Pres.I.E.E., M.Inst.C.E. Council — George Beilby; Bertram Blount; A. G. Charleton, Pres.I.M.M.; W. R. Cooper, M.A., B.Sc.; Sherard Cowper-Coles; F. G. Donnan, M.A., Ph.D.; Prof. A. K. Huntington; R. A. Lehfeldt, D.Sc.; F. Mollwo Perkin, Ph.D.; W. S. Squire, Ph.D.; O. J. Steinhart, Ph.D. Intending members are requested to send their names to the Hon. Sec., Mr. F. S. Spiers, 82, Victoria Street, S.W.

Science Abstracts.—We are informed that *Science Abstracts* will be published in future in two sections:—*Section* A.—Physics, embracing Light, including Photography, Heat, Sound, Electricity and Magnetism, Chemical Physics and Electro-chemistry, General Physics, Meteorology and Terrestrial Physics, Physical Astronomy. *Section* B.—Embracing Steam Plant, Gas and Oil Engines, Automobiles, Oil Engine driven ships and launches, Balloons and Air-ships, General Electrical Engineering, including Industrial Electro-chemistry, Electric Generators, Motors, and Transformers, Electrical Distribution, Traction and Lighting, Telegraphy and Telephony. We understand that the American Physical Society is now joined with the Institution of Electrical Engineers and the Physical Society of London in the direction of the publication, and has elected Professor E. H. Hall, of Harvard University, as its representative on the publishing Committee.

The Batavian Society of Experimental Philosophy of Rotterdam.—At the General Meeting of this Society on September 20th, 1902, a number of questions were proposed for solution, and a prize offered for the answer to one or more which may be judged the best. The questions, 49 in number, include all kinds of scientific subjects of interest. The prize offered is the Society's Gold Medal weighing 30 ducats, or its equivalent value (about £14), at the option of the winner. Answers must not be in the handwriting of the competitors, but must be marked with a distinctive motto, and accompanied by a sealed packet containing a copy of the motto, and the name and address of the sender, and must be sent to the Secretary, Dr. G. J. W. Bremer, at Rotterdam, by February 1st, 1904.

Ferric Oxide and its Hydrates.—O. Ruff.—The author constructed a small block of steel having a cavity lined with copper; it was closed with a screw enabling a pressure of 5000 atmospheres to be applied. In this cavity he placed water (either pure or containing different salts), holding precipitated ferric hydrate in suspension; the apparatus was closed and the pressure applied, and the whole exposed for several days to known temperatures up to 100°. Under these conditions the red colloidal hydrate was converted, after about twenty days, into limonite or rust, $Fe_2O_3.\frac{3}{2}H_2O$, if the temperature was kept below 42·5°, while with a temperature between 42·5° and 62·5° gœthite, $Fe_2O_3.H_2O$, was obtained, and at temperatures above 62·5°, hydrohæmatite, $Fe_2O_3.\frac{1}{2}H_2O$; in fact, the formation of these different hydrates depends on the vapour tension of the water-vapour. But under the ordinary pressure the red colloidal hydrate should be doubtless first completely dehydrated before coming to the state of limonite, which is the only really stable hydrate.—*Berichte*, vol. xxxiv. p. 3417.

MEETINGS FOR THE WEEK.

MONDAY, 16th.—Society of Arts, 8. (Cantor Lectures). "Paper Manufacture," by Julius Hübner.

TUESDAY, 17th.—Royal Institution, 5. "The Physiology of Digestion," by Prof. Allan Macfadyen, M.D.

—— Society of Arts, 8. "Heraldry in Decoration," by George W. Eve, A.R.E.

WEDNESDAY, 18th.—Society of Arts, 8. "Three-colour Printing," by Harvey Dalziel.

—— Chemical, 5 30. "The Molecular Re-arrangement of N-Substituted Imino-ethers" and "The Nature and probable Mechanism of Metal Replacement in Tautomeric Compounds," by G. D. Lander. "The Chlorine Derivatives of Pyridine—Part VIII., The Interaction of 2 : 3 : 4 : 5-Tetrachlorpyridine with Ethyl Sodiomalonate," by W. J. Sell and F. W. Dootson. "The Biological Method for resolving Inactive Acids into their Optically Active Components," by A. McKenzie and A. Harden.

THURSDAY, 19th.—Royal Institution, 5. "Arctic and Antarctic Exploration," by Sir Clements Markham, K.C.B., F.R.S.

FRIDAY, 20th.—Royal Institution, 9. "The Measurement of Energy," by Principal E. H. Griffiths, Sc.D., F.R.S.

SATURDAY, 21st.—Royal Institution, 3. "Dramatic Criticism," by Arthur B. Walkley.

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THE CHEMICAL NEWS.

Vol. LXXXVII., No. 2255.

REVISION OF THE ATOMIC WEIGHT OF LANTHANUM.*

By BOHUSLAV BRAUNER, Ph.D., and FRANTIŠEK PAVLÍČEK, Bohemian University, Prague.

(Concluded from p. 74).

Third Method of Atomic Weight Determination.

In 1882, Stolba (*Abhandl. Königl. Böhm. Ges. Wissensch.*) proposed a new method for the determination of the atomic weight of lanthanum and other rare earth elements (Ce, Di). In one part of the dry oxalate the percentage of R_2O_3 (or CeO_2) is determined by calcination, and in another that of C_2O_3, with permanganate in sulphuric acid solution.† This method was described for a second time as new by W. Gibbs in 1893 (*Proc. Amer. Acad.*, xxviii., 260). Lanthanum material was purified by Shapleigh by the Mendeleeff-Auer method, and the oxalate washed with a large quantity of hot water. The oxalates were dried on a water-bath, and then thoroughly mixed. The mean atomic weight of lanthanum found by this method by Gibbs was La = 139·70. Gibbs states that Dr. Shapleigh found, with the same material by the sulphate method, La = 139·71.

Stolba's method was used by me with very good results for the determination of the atomic weights of cerium, thorium, and praseodym, and I thought, therefore, that it might serve as a method of control in the case of lanthanum. But it was necessary to consider the question whether the lanthanum material used by Gibbs really contained an earth with a much higher atomic weight, or whether the composition of his oxalate was abnormal.

The Fractions La o to La 7, into which our purest lanthanum material had been divided, were thrown down as oxalates by adding an excess of pure oxalic acid to a hot dilute solution of lanthanum nitrate. After pouring off the supernatant liquid, the precipitate was digested with oxalic acid solution. A perforated round platinum plate, 2 c.m. in diameter, covered with a slightly larger piece of smooth round filter-paper, was used for collecting the oxalate on the pump. It was washed, first with dilute oxalic acid solution, then with *cold*, *tepid*, or *hot* water, which mode of washing has an influence on the composition of the precipitate, as will be noticed further on, and finally with pure alcohol rectified in the presence of tartaric acid.

Oxalates prepared in this way may be obtained perfectly *air dry* and *homogeneous* after standing for a few hours in the open air (covered with paper), an important circumstance when different portions are to be weighed out for different determinations. These conditions are not fulfilled when the oxalates are dried on the water-bath as recommended by Gibbs.

In converting the oxalate into the oxide, it must be heated very gently and gradually, beginning from the lid in order to avoid a loss of the fine powder which is easily carried away with the escaping gases. It appears, however, that it is sometimes difficult to obtain a perfectly pure oxide as soon as its quantity exceeds 1 grm., and the "personal error" due to two different observers may not be without influence on the slight deviations in the percentage of oxide from the same oxalate.

For the determination of the oxalic radicle, C_2O_3, the oxalate was heated in an Erlenmeyer flask with 50 c.c. of 12 per cent sulphuric acid and titrated with permanganate with special precautions into which I cannot enter here. The permanganate was standardised many times with ammonium oxalate under exactly the same conditions. The salt was repeatedly re-crystallised from hot water, finally in the presence of free ammonia, in order to prevent the formation of the acid salt. The results are given in Table V.

The differences between the atomic numbers obtained are very considerable, being equal to a maximum of 1·25, and yet, after excluding the abnormal results obtained with Fraction La 4, a mean value La = 139·07 is found, identical with the true atomic weight of lanthanum.

The differences are due to the different composition of the individual oxalates, and this depends on the temperature of the water used for washing them. With an increase in the temperature of the water, the quantity of the water of crystallisation of the oxalates is found to diminish and the atomic number to rise, as is seen from Table VI.

The abnormal composition of the oxalate is most prominent in Fraction La 7, which yielded the atomic number La = 139·66. The oxalate was washed with hot water, and formed a heavy crystalline powder. It must have consisted partly of a basic oxalate, which was probably formed by the hydrolysis of an oxalonitrate.

As this number is identical with that obtained by Gibbs, namely, La = 139·7, from an oxalate which was prepared exactly in the same way, it is unnecessary to assume that this number represents the real atomic weight of lanthanum contained in the material used by him.

On the other hand, the abnormally low results obtained in our series from the oxalates washed with cold water, namely, La 1, La 5, and La 6, point to the presence of free oxalic acid in the oxalates used, undoubtedly due to absorption.

A normal atomic number was obtained, probably by chance only, from the fractions La o and La 3.

An examination of the same lanthanum material which, in Dr. Shapleigh's hands, gave the abnormally high number La = 139·7 by the sulphate method, and which was presented to me by him, has shown that this material is not quite free from foreign earths, especially from traces of the constituents of didymium, so that even this high number finds an explanation.

It is seen from Table VI. that pure precipitated lanthanum oxalate very probably contains 11 mols. of water, as stated by Wyrouboff (*Bull. Soc. Franc. Min.*, 1895, xxiv., 110), who also prepared an oxalate with $3H_2O$.

I obtained (*Trans.*, 1898, lxxiii., 974) by crystallisation from dilute sulphuric acid an oxalate with $7H_2O$, but the existence of a salt with $9H_2O$ as found by Czudnowicz and Cleve becomes improbable. It would seem that in fraction La 4 an oxalate with $6H_2O$ was present.

Is Lanthanum a Mixture of Elements?

The results of the present investigation enable me to answer this question as follows:—

1. Lanthanum material purified (*a*) by fractional crystallisation and re-crystallisation of its soluble salt with ammonium nitrate (Mendeléeff-Auer), (*b*) by fractional fusion with potassium and sodium nitrates at 450—500° (Debray-Schützenberger), and (*c*) split up into eight different fractions by partial precipitation with potassium hydroxide, contains only *one element*, the true lanthanum with the atomic weight La = 139·04 in a vacuum. The least basic fractions (especially La 7) may contain a slight admixture of an element with a higher atomic weight, which gives to the oxide a very pale buff tint, but this very small quantity has scarcely any influence on the atomic weight.

2. An element with the atomic weight 135, which was presumably found by some chemists, lastly by Schützenberger in 1895 in some fractions of lanthanum, *is not contained* in the pure lanthanum or in any of its side fractions, and it must be definitely stated that this low number could

* From the *Transactions of the Chemical Society*, 1902, vol. lxxxi.

† In this paper, Stolba finds for the first time that lanthanum oxide may be determined alkalimetrically with a good result.

TABLE V.—*Analyses of Lanthanum Oxalate.*

No. of experiment.	No. of fraction.	Lanthanum oxalate. Grms.	La_2O_3. Grms.	La_2O_3. Per cent.	C_2O_3. Grm.	C_2O_3. Per cent.	Ratio used for calculation.	Atomic weight* La =
31.	La 0	(*a*) 2·27247	1·06543	46·884	—	—	*a* : *c*	139·12
		(*b*) 2·14773	1·00676	46·876	—	—	*b* : *c*	139·09
		(*c*) 0·67462	—	—	0·20941	31·041	—	—
32.	La 1	(*a*) 2·0854	0·93205	44·722	—	—	*a* : *f*	138·77
		(*b*) 1·8823	0·8416	44·711	—	—	*b* : *f*	138·74
		(*c*) 1·92285	0·85993	44·694	—	—	*c* : *f*	138·67
		(*d*) 2·51643	1·12533	44·719	—	—	*d* : *f*	138·76
		(*e*) 3·80470	1·70246	44·746	—	—	*e* : *f*	138·86
		(*f*) 1·60083	—	—	0·47097	29·673	—	—
33.	La 2	(*a*) 1·7485	0·7847	44·879	—	—	*a* : *c*	138·90
		(*b*) 1·7983	0·80645	44·845	—	—	*b* : *c*	138·77
		(*c*) 1·30665	—	—	0·38879	29·755	—	—
34.	La 3	(*a*) 2·2325	1·0760	48·197	—	—	*a* : *b*	139·07
		(*b*) 1·14021	—	—	0·36395	31·920	—	—
35.	[La 4]	[(*a*) 2·1266]	[1·0683]	[50·235]	—	—	*a* : *c*	[138·94]
		[(*b*) 2·56509]	[1·28627]	[50·145]	—	—	*a* : *d*	[138·70]
		[(*c*) 1·24241]	—	—	[0·41368]	[33·297]	*b* : *c*	[138·65]
		[(*d*) 1·08010]	—	—	[0·36017]	[33·346]	*b* : *d*	[138·41]
36.	La 5	(*a*) 1·9488	0·8721	44·751	—	—	*a* : *b*	138·79
		(*b*) 0·89926	—	—	0·26698	29·689	—	—
37.	La 6	(*a*) 2·0880	0·9755	46·719	—	—	*a* : *c*	139·38
		(*b*) 1·9684	0·9188	46·678	—	—	*b* : *c*	139·24
		(*c*) 1·41521	—	—	0·43706	30·883	—	—
38.	La 7	(*a*) 1·9753	0·9507	48·129	—	—	*a* : *d*	139·65
		(*b*) 2·0111	0·9677	48·118	—	—	*b* : *d*	139·61
		(*c*) 2·21199	1·06469	48·133	—	—	*c* : *d*	139·66
		(*d*) 1·13639	—	—	0·36094	31·762	—	—
		Mean atomic weight after rejecting the results of Experiment 35 (La 4)						139·07

* When O=16, C=12·00, and N=14·04.

TABLE VI.—*Showing the Percentage Composition of the different Fractions of Lanthanum Oxalate, &c.*

Fraction..	La 1.	La 5.	La 2.	La 6.	La 0.	La 7.	La 3.	[La 4.]
La_2O_3 per cent	44·72	44·75	44·86	46·70	46·88	48·13	48·20	[50·19]
C_2O_3 per cent	29·67	29·69	29·76	30·88	31·04	31·76	31·92	[33·32]
H_2O per cent	25·61	25·60	25·38	22·42	22·08	20·11	19·88	[16·49]
Mols. H_2O	10·37	10·34	10·24	8·69	8·53	7·57	7·47	[5·95]
La, minimum	138·67	138·79	138·77	139·24	139·09	139·61	139·07	[138·41]
La, maximum	138·86	—	138·90	139·38	139·12	139·66	—	[138·94]

only be obtained from fractions which contained yttria, as shown by my chemical and optical experiments.

3. With regard to the fact that the least basic fractions, obtained from our lanthanum material by the second method of fractionation, yielded by the correctly applied sulphate method the numbers $R^{III}=139·27$ (experiment 14) and 139·20 (experiment 27), whilst the solution of this earth was perfectly free from any earth possessing an absorption spectrum, the conclusion may be drawn that in these fractions a small quantity of an element with a higher atomic weight than that of lanthanum is present.

This fact stands in the closest relation with that discovered by me twenty years ago (*Monatsh.*, 1882, iii., 486), that on fractionating the mixture of lanthanum and old didymium with ammonia, intermediate fractions, less basic than lanthanum, are obtained containing an element with a higher atomic weight than that of lanthanum. The numbers obtained from these fractions were $R^{III}=140·19$ and the maximum $R^{III}=140·63$. In the spark spectrum, new lines not belonging to lanthanum were observed.

These experiments were given up at that time for this reason: Cleve (*Bull. Soc. Chim.*, 1883, xxxix., 289) declared with the whole weight of his authority that between lanthanum and didymium no third element is contained. In this conclusion he was evidently wrong, and the question requires a new and thorough investigation.

Critical Remarks.

On casting a glance at the atomic weight determinations collected in Table I. in the introduction, the following explanation of the discrepancies may be offered:—

(i.). The determinations by Rammelsberg and Marignac (1), (2), and (3), and Holzmann (1) are founded on the precipitation of barium sulphate, which carries down a considerable quantity of lanthanum sulphate.

(ii.). Holzmann's determinations (2) and (3) are made from somewhat complicated salts.

(iii.). As regards the determinations of Czudnowicz and Erk (2), see (i.).

(iv.). Hermann's determinations (1), (2), and (3) are very near the truth, but a little high, probably because his lanthanum was not freed from its higher companion.

(v.). The numbers of Zschiesche, Erk (1) and Erk 2) are too low, very probably owing to the presence of yttria.

(vi.). Marignac's number (4) is too low owing to the very hygroscopic nature of the anhydrous sulphate and incomplete expulsion of water from the anhydrous salt.

(vii.). Cleve's number (1) is identical with that obtained by us from the fraction A5+6; see also (iv.).

(viii.). The numbers obtained by Gibbs and Shapleigh have been explained in an earlier section of this paper.

(ix.). The low numbers obtained by Brauner (1) and (2), Cleve (2), Bauer, Bettendorff, and probably by Schützenberger and Muthmann (although the last two chemists give no details about their work) are due to the formation of some acid sulphate and to the very hygroscopic nature of the anhydrous sulphate.

Having shown that the majority of the determinations of the atomic weight of lanthanum hitherto made are inexact, either because the material used was not quite pure or homogeneous, or because the method used for the determination was not free from error, the following important question arises:—

Are we entitled to use the whole series of determinations hitherto made for the final calculation, or may we not regard the number resulting from the present minute and detailed work, namely, La=139·04, as lying near the true atomic weight of lanthanum, awaiting, of course, its confirmation by other methods?

In conclusion, I may say that, having extended the research to other rare earths and their sulphates, I find this:—*All atomic weight determinations of the rare earth elements made by the synthetical sulphate method during the nineteenth century are vitiated by an error which tends to lower the atomic weight and diminishes as the basicity of the earth decreases.*

If the atomic weight of lanthanum is La=139·04, it is highly improbable that cerium would possess the same atomic weight, Ce=139, as assumed by Clarke from the result of the work of Wyrouboff and Verneuil, who obtained for a "bivalent" cerium the value Ce=92·7. This assumption has been proved to be correct by work specially done in our laboratory.

EXPERIMENTS ON THE PRODUCTION OF SULPHURETTED HYDROGEN IN ALCOHOLIC FERMENTATION.

By M. and E. POZZI-ESCOT.

If we add sulphur or a sulphate to a must in alcoholic fermentation, sulphuretted hydrogen is produced during the fermentation. This is due to the intervention of a reducing diastase called philothion.

It was of interest to ascertain at what particular moment of the fermentation the sulphuretted hydrogen was produced; that is to say, the diffusion of the reducing diastases.

One hundred grms. of compressed brewery yeast were taken, and—

1. After a series of washings the yeast was placed in a 1 litre flask containing water and 10 per cent of saccharose; this was shaken vigorously to get the yeast thoroughly spread throughout the mass, and the liquid was divided into two equal parts.

2. One portion of the liquor was placed in a flask and treated with an excess of flowers of sulphur, previously triturated with water, and well shaken; it was then left to stand at 25°, and, thanks to the preceding operations, it entered rapidly into fermentation; it was shaken up occasionally to help the fermentation, and sulphuretted hydrogen was tested for systematically during the progress of the operation; in this manner we found that it is towards the end of the time, when still a sixth part of the total sugar remained, that the sulphur is attacked to a noticeable extent.

3. The second portion was placed in a parchment paper diffuser, and the whole placed in a crystallising dish containing water, but as little water as possible should be used.

The object of this experiment is to ascertain the moment when the yeast diffuses its reducing diastase; to detect this in the apparatus, we made use of peroxide of hydrogen, which is a very sensitive reagent, as I have shown previously. Under these conditions we observe that the sucrose of the yeast commences to diffuse at the commencement of the experiment, but that it is only towards the end that the reducing diastase appears.

4. The conclusion arrived at from these experiments is that normally yeast does not let its reducing diastases exude, but that they are diffusible as soon as the vegetable ferment meets with an obstacle to its evolution; that is, with more or less paralysing substances; in a word, that during its active life the yeast retains its reducing elements, but that these enter into solution as soon as the fermenting power has reached its maximum, when the yeast is affected and ceases to be reproduced freely.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 13.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, January 21st, 1903.

Prof. J. Emerson Reynolds, Sc.D., F.R.S., President, in the Chair.

(Concluded from p. 82).

9. "*Synthesis of Imino-ethers. N-Ethyl-, N-Methyl-, and N-Benzylbenziminoethers.*" By G. D. Lander.

Alkylation by means of silver oxide and alkyl iodides occurs to a very limited extent with the alkyl and benzyl benzamides, and the imino-ethers were therefore prepared from the imide chlorides by means of the sodium alkyloxides (*Trans.*, 1902, lxxxi., 591). The *N*-ethyl and *N*-methyl derivatives are contaminated with compounds of higher boiling-points containing a smaller percentage of carbon, which may be ortho-compounds of the type $CPh(OR)_2NHR'$. The purification of the imino-ethers is effected by warming with 1/10 molecule of acetic anhydride.

The *imide chloride* of *benzethylamide*, CPhCl:NEt, boils at 110—111° (15 m.m.), and gives, on treatment with aniline, *ethylphenylbenzenylamidine*, CPh(:NEt)·NHPh; this base, which melts at 74—76°, is also obtained by condensing aniline with the imino-ether; its platinichloride crystallises with $2H_2O$, and melts at 204°

N-Ethylbenzimino-ethyl ether, CPh(OEt):NEt, and *N-ethylbenziminomethyl ether*, CPh(OMe):NEt, boil at 105° and 97—100° under 11 m.m. pressure, and at 221—223° and 209—212° (uncorr.) under the ordinary pressure, respectively; they are colourless, limpid liquids of amine like odour.

Benzoyldiethylbenzenylamidine, CPh(:NEt)·NEt·COPh, a basic by-product of the imino-ether synthesis, crystallises in colourless prisms melting at 90—91·5° without decomposition; its *platinichloride* melts at 151—151·5°, and its solution, in dilute hydrochloric acid, gradually decomposes with the formation of benzoic acid, ethylamine, and a compound (m. p. 101—102°) not yet examined.

N-Methylbenziminomethyl ether, CPh(OMe):NMe, boils at 94—95° under 12 m.m., and at 203—206° (uncorr.) under the ordinary pressure; the crude hydrochloride melts at 65—70°, regenerating benzmethylamide.

N-Methylbenziminoethyl ether, CPh(OEt):NMe, was not obtained pure; it boils at about 105° under 14 m.m., and at about 215° under the ordinary pressure.

Benzoyldimethylbenzenylamidine,—

$$CPh(:NMe)\cdot NMe\cdot COPh,$$

which resembles the diethyl compound in crystalline form and properties, melts at 116—117·5; its *platinichloride* melts at 184—185°.

The *imide chloride of benzbenzylamide*, $CPhCl:NCH_2Ph$ (compare *Ber.*, 1897, xxx., 1788), decomposes, almost completely, on distillation into benzonitrile and benzyl-chloride, but the undistilled imide chloride condenses with aniline, yielding *phenylbenzylbenzenylamidine*, $CPh(:NCH_2Ph)\cdot NHPh$, which melts at 99—100°, and is identical with Beckmann and Fellrath's base obtained from benzphenylamide imide chloride and benzylamine, and also with the amidine formed by condensation of *N*-benzylbenzimino-ethyl ether with aniline. *Phenylmethyl-benzylbenzenylamidine*, $CPh(:NCH_2Ph)\cdot NMePh$, which is produced either from methylaniline and the imide chloride of benzbenzylamide, or by alkylating the above described amidine with methyl iodide, melts at 89—90°.

N-Benzylbenzimino-ethyl ether, $CPh(OEt):NCH_2Ph$, is a viscid, colourless, odourless oil, boiling at 186—188° under 12 m.m. pressure; the corresponding *methyl ether*, $CPh(OMe):NCH_2Ph$, boils at 178—180° under 11 m.m. pressure. These *N*-benzylbenzimino ethers, when left in contact with air, undergo oxidation to dibenzamide.

10. "*The Condensation of Phenyl Ethyl Ketone (Propiophenone) with Benzalacetophenone and of Acetophenone with Benzalpropiophenone.*" By R. D. Abell.

Phenyl ethyl ketone and benzalacetophenone condense under the influence of sodium ethoxide to form (i.) 2-phenyl-1-methyl-1:3-dibenzoylpropane, $C_{24}H_{22}O_2$ (prisms, m. p. 103·5—104·5°); (ii.) 2:4-diphenyl-1-methyl-1:3:5-tribenzoylpentane, $C_{39}H_{34}O_3$ (rhombic plates, m. p. 241—242°).

The former substance reacts with hydroxylamine to form a *dioxime*, $C_{24}H_{24}N_2O_2$ (needles, m. p. 204—205°), and with hydroxylamine hydrochloride to form 2:4:6-*triphenyl*-3 *methylpyridine*, $C_{24}H_{19}N$ (needles, m. p. 141—142°), this base yielding a *picrate* (yellow prisms, m. p. 190—191°) and a *hydrochloride* in colourless, hygroscopic needles.

Acetophenone and benzalpropiophenone in presence of sodium ethoxide react to form: (i.) 2-phenyl-1:3-dimethyl-1:3-dibenzoylpropane, $C_{25}H_{24}O_2$ (six-sided crystals, m. p. 162—163°, *Trans.*, 1901, lxxix., 936); (ii.) a mixture of 2-phenyl-1:3-dibenzoylpropane, $C_{23}H_{20}O_2$ (Kostanecki and Rossbach, *Ber.*, 1896, xxix., 1492), and 2-phenyl-1-methyl-1:3 dibenzoylpropane, $C_{24}H_{22}O_2$, crystallising in prisms melting at 93—94°; (iii.) 2-phenyl-1-methyl-1:3-dibenzoylpropane, $C_{24}H_{22}O_2$ (prisms, m. p. 103·5—104·5°); (iv.) 2:4-diphenyl-1-methyl-1:3:5-tribenzoylpentane, $C_{39}H_{34}O_3$ (rhombic plates, m. p. 241—242°); (iv.) 2:4-diphenyl-1-methyl-1:3:5-tribenzoylpentane, $C_{39}H_{34}O_3$ (rhombic plates, m. p. 241—242°); (v.) 2:4-diphenyl-1:3:5-tribenzoylpentane, $C_{38}H_{32}O_3$ (glistening prisms, m. p. 255—256°) (Kostanecki and Rossbach, *Ber.*, 1896, xxix., 1492); (vi.) benzoic acid; (vii.) a pink, viscid, acid liquid.

The two homologous 1:5-diketones indicated under (ii.) could not be separated by solvents, but were identified by means of the corresponding dioximes and pyridines, namely, the dioxime, $C_{23}H_{22}N_2O_2$ (needles, m. p. 163—164°), and 2:4:6-triphenylpyridine, $C_{23}H_{17}N$ (needles, m. p. 137—138°, Wislicenus and Newman, *Annalen*, 1898, cccii., 236), corresponding to 2-phenyl-1:3-dibenzoyl-propane, and the dioxime, $C_{24}H_{24}N_2O_2$ (needles, m. p. 204—205°) and 2:4:6-triphenyl-3-methylpyridine, $C_{24}H_{19}N$ (needles, m. p. 141—142°), corresponding to 2-phenyl-1-methyl-1:3-dibenzoylpropane.

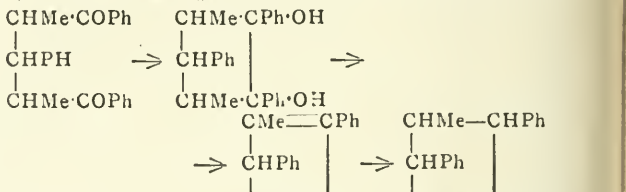
In presence of an alcoholic solution of sodium hydroxide, acetophenone and benzalpropiophenone reacted to form (i.) 2-phenyl-1:3-dimethyl-1:3-dibenzoylpropane, $C_{25}H_{24}O_2$ (six-sided crystals, m. p. 162—163°); (ii.) the mixture of homologous 1:5-diketones (prisms, m. p. 93—94°).

It is therefore evident that the reaction between acetophenone and benzalpropiophenone is not a condensation in the true sense of the word, and that the substances isolated are formed by the condensation of the decomposition products of benzalpropiophenone (phenyl ethyl ketone and benzaldehyde) with benzalpropiophenone and acetophenone.

11. "*A Synthesis of 1:3:5-Triphenyl-2:4-Dimethylcyclopentane and of 1:3:5-Triphenyl-2-methylcyclopentane.*" By R. D. Abell.

2-Phenyl-1:3-dimethyl-1:3-dibenzoylpropane, $C_{25}H_{24}O_2$ (*Trans.*, 1901, lxxix., 936), when reduced by zinc dust and acetic acid, yielded the cyclic pinacon 1:3:5-triphenyl-2:4-dimethyl*cyclo*pentandiol, $C_{25}H_{26}O_2$ (prisms, m. p. 143—144°), and this on reduction with red phosphorus and hydriodic acid gave two isomeric 1:3:5-triphenyl-2:4-dimethyl*cyclo*pentanes, $C_{25}H_{26}$, the one crystallising in needles, m. p. 80—81°, the other being a yellow oil (b. p. 246—248°, 25 m.m.).

When fused with oxalic acid, the pinacone loses two molecules of water (Fischer, *Ber.*, 1897, xxx., 559) to form the unsaturated hydrocarbon, 1:3:5-triphenyl-2:4-dimethyl*cyclo*pentadiene, $C_{25}H_{22}$ (needles, m. p. 127—128°), which, on reduction with red phosphorus and hydriodic acid, also gave both saturated hydrocarbons.

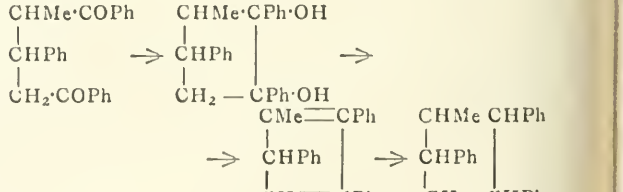


2-Phenyl-1-methyl-1:3 dibenzoylpropane, $C_{24}H_{22}O_2$, on reduction with zinc dust and acetic acid gave (i.) 1:3:5-triphenyl-2-methyl*cyclo*pentandiol, $C_{24}H_{24}O_2$; (ii.) 1:3:5-triphenyl-2-methyl*cyclo*pentadiene, $C_{24}H_{20}$; the former is a brown oil crystallising with difficulty; the latter, which is probably due to the dehydration of the cyclic pinacone by acetic acid, forms yellow needles, and melts at 162—163°.

The cyclic pinacone, $C_{24}H_{24}O_2$, obtained as an almost colourless oil by reducing the 1:5-diketone with sodium amalgam in moist ethereal solution, solidified in needles (m. p. 68—80°) when left in a vacuum over concentrated sulphuric acid, but could not be re-crystallised from solvents as it always separated as an oil.

The cyclic pinacone, when fused with oxalic acid, gave the unsaturated hydrocarbon, 1:3:5-triphenyl-2 methyl-*cyclo*pentadiene, $C_{24}H_{20}$ (yellow needles, m. p. 162—163°).

Both the pinacone and the unsaturated hydrocarbon gave two isomeric 1:3:5-triphenyl-2-methyl*cyclo*-pentanes, $C_{24}H_{20}$, on reduction with red phosphorus and hydriodic acid, the one crystallising in needles (m. p. 121—122°), the other being a yellow oil (b. p. 260—262°, 28 m.m.).



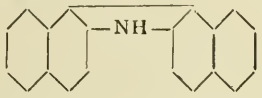
12. "*Formation of Carbazoles by the Interaction of Phenols, in the Orthoketonic Form, with Arylhydrazines.*" By F. R. Japp and W. Maitland.

In a preliminary note (*Proc.*, 1901, xvii., 176) the authors showed that carbazoles could be obtained by heating certain phenols with arylhydrazines in presence

of their hydrochlorides. They now find that the ease with which this reaction occurs is proportional to the readiness with which the phenol in question passes into the tautomeric orthoketonic form. Thus phenol iteelf does not yield any carbazole under the foregoing conditions; α-naphthol reacts, but with great difficulty, giving a very poor yield of the carbazole derivative; β naphthol and 9-hydroxyphenanthrene react with relative ease. This is precisely the order of reactivity in the orthoketonic form, which Thiele's theory of double linkings would, in its application to benzene derivatives, predict for these phenols.

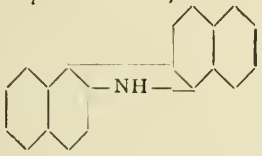
In addition to the carbazoles described in the preliminary note, the following have been prepared. The nomenclature adopted is that proposed by Graebe (Ber., 1894, xxvii., 3066).

s-1 : 2-*Dinaphthocarbazole*,—



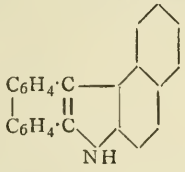
(m. p. 155°).—From β-naphthol, β-naphthylhydrazine and its hydrochloride; identical with "dinaphthyleneamine," which Walder (*Ber.*, 1882, xv., 2173) obtained by heating ββ-dinaphthol with the double compound of zinc chloride and ammonia.

1 : 2 : 2' : 1'-*Dinaphthocarbazole*,—



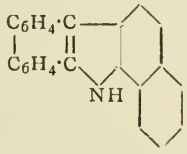
(m. p. 231°).—From β-naphthol, α-naphthylhydrazine and its hydrochloride.

9 : 10-*Phenanthro*-1' : 2'-*naphthocarbazole*,—



(m. p. 220°).—From 9-hydroxyphenanthrene, β-naphthylhydrazine and its hydrochloride.

9 : 10-*Phenanthro*-2' : 1'-*naphthocarbazole*,—

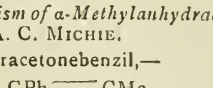


(m. p. 225·5°).—From 9-hydroxyphenanthrene, α-naphthyl, hydrazine, and its hydrochloride.

In their first note an this subject (*loc. cit*,) the authors pointed out that 1 : 2-naphthocarbazole (phenyl-2-naphthylcarbazole), first prepared by Schöpff (*Ber.*, 1896, xxix, 269), melted at 134—135°, instead of, as stated by that investigator, at 120°. They had overlooked the fact that this correction had already been made by F. Ullmann (*Ber.*, 1898, xxxi., 1697).

13. "*Dimorphism of α-Methylanhydracetonebenzil*." By F. R. Japp and A. C. Michie.

α-Methylanhydracetonebenzil,—



which is best obtained by the condensation of benzil with methyl ethyl ketone under the influence of a 0·5 per cent solution of potassium hydroxide in absolute alcohol, was described by Japp and Meldrum (*Trans.*, 1901, lxxix, 1029) as forming large, flat crystals of rhombic outline ("lozenge-shaped") melting at 118°. These crystals show oblique extinction in polarised light.

The authors prepared this compound on various occasions, and were able to confirm the foregoing observations. About a year ago, however, although working under apparently the same conditions, they obtained a substance crystallising in octahedra which were isotropic in polarised light, and melted at 133·5°. Analysis showed that this substance had the same composition as α-methylanhydracetonebenzil.

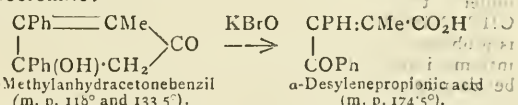
Further investigation has demonstrated that these two substances, which the authors at first supposed to be distinct chemical compounds, are, in reality, merely dimorphous forms of α-methylanhydracetonebenzil. The difficulty in proving this lay in the fact that, after the second form had once been obtained, it was apparently impossible again to prepare the first form. At last, however, the authors succeeded in doing this, but they were quite unable to obtain the result a second time; moreover, the substance was so unstable that it was converted, even in determining its melting-point, into the less fusible form.

The authors wish to call attention to this dimorphism, as other investigators, who might happen to obtain the more stable form first, would probably fail to recognise the substance as chemically identical with that formerly described (*Trans.*, *ibid.*).

14. "*The Oxidation Products of the Methyl Homologues of Anhydracetonebenzil*." By F. R. Japp and A. C. Michie.

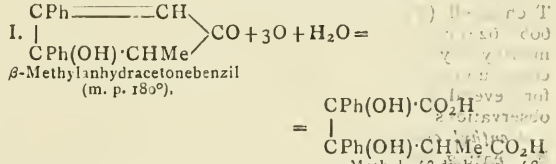
The various methyl homologues of anhydracetonebenzil were described by Japp and Meldrum (*Trans.*, 1901, lxxix, 1028, 1036, and 1037). The present authors have studied the oxidation of these substances, with the exception of αββ-trimethylanhydracetonebenzil, which, owing to the difficulty of preparing it, was not included in the investigation.

Of the four methyl homologues examined, only α-methylanhydracetonebenzil is attacked by alkaline hypobromite:—

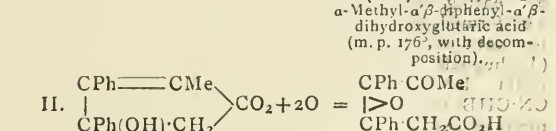


α-Methylanhydracetonebenzil (m. p. 118° and 133·5°). α-Desyleneпropionic acid (m. p. 174·5°).

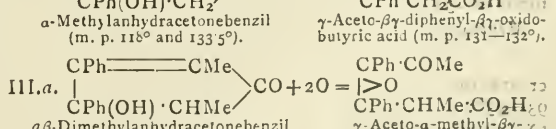
All four homologues are, however, readily oxidised by chromium trioxide in acetic acid solution:—



β-Methylanhydracetonebenzil (m. p. 180°). α-Methyl-α'β-diphenyl-α'β-dihydroxyglutaric acid (m. p. 176°, with decomposition).



α-Methylanhydracetonebenzil (m. p. 118° and 133·5°). γ-Aceto-βγ-diphenyl-β$_1$-oxidobutyric acid (m. p. 131—132°).



αβ-Dimethylanhydracetonebenzil (m. p. 150°). γ-Aceto-α-methyl-βγ-diphenyl-βγ-oxobutyric acid (m. p. 164°, with decomposition).

III.*b*. $CPh{=}{=}CMe$ / $CPh(OH)\cdot CHMe$ $>CO + O + H_2O$ =

$\alpha\beta$-Dimethylanhydracetonebenzil.

$= CPh(OH)\cdot CMe(OH)$ / $CPh(OH)-CHMe$ $>CO$

1 : 3-Dimethyl-4 : 5-diphenyl-1 : 4 : 5-trihydroxy*cyclo*pentanone-(2) (m. p. 89°).

IV. $CPh{=}{=}CH$ / $CPh(OH)\cdot CMe_2$ $>CO + 3O$ = $CPh\cdot CO_2H$ / $>O$ / $CPh\cdot CMe_2\cdot CO_2H$

$\beta\beta$-Dimethylanhydracetonebenzil (m. p. 181°).

$\alpha\alpha$-Dimethyl-$\alpha'\beta$-diphenyl-$\alpha'\beta$-oxidoglutaric acid (m. p. 171° and 184°).

The authors suggest the use of the prefix "oxido" to denote "bridge-oxygen" regarded as a bivalent substituent.

15. "*Action of Hypobromites on Amides.*" By A. Lapworth and W. W. S. Nicholls.

The action of hypobromites on certain amides has been carefully studied with the idea that the change might depend on the formation, at an intermediate stage, of alkyl and cyanate ions, which would subsequently unite to form an alkyl carbimide, as indicated in the following equations :—

$$CH_3\cdot CO\cdot NH_2 + Br_2 = \overset{+}{C}H_3 + \overset{-}{C}NO + 2HBr,$$

$$\overset{+}{C}H_3 + \overset{-}{C}NO = CH_3\cdot N{:}C{:}O.$$

In endeavouring to imitate the conditions supposed to obtain during the reaction, potassium cyanate was warmed with potassium methyl sulphate in alkaline solution; methylamine was easily isolated, but in comparatively small amount. It is well known that phenylcarbimide is formed when nascent phenyl groups (ions ?) are produced in presence of potassium cyanate, as when benzenediazonium salts are decomposed by copper powder.

An examination was made of the by-products in the preparation of methylamine from acetamide and of aniline from benzamide, particular attention being paid to the possibility of methyl alcohol and phenol or their decomposition products being formed, but no direct evidence bearing on the point was obtained. From benzamide, under these conditions, benzyldenedibenzamide, $CHPh(NHCOPh)_2$, is almost invariably obtained. This is probably not produced from benzaldehyde formed at an intermediate stage, as the aldehyde does not condense with benzamide under the experimental conditions.

16. "*Derivatives of Menthyl Cyanoacetate.*" By D. A. Bowack and A. Lapworth.

A recent abstract (1903, lxxxiv., ii., 2) of a paper by Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1902, xxxiv., 606–622) contains a reference to the optical rotation of menthyl cyanoacetate. As the authors have had this compound and some of its derivatives under examination for several months, they wish to record certain of their observations.

Menthyl cyanoacetate, $CN\cdot CH_2\cdot CO_2\cdot C_{10}H_{19}$, prepared by heating the ethyl ester with menthol, crystallises in well-formed, flattened needles melting at 83–84°. In 2 per cent solution in benzene, it had $[\alpha]_D = -81{\cdot}12°$ (Tschugaeff gives $-87{\cdot}71°$) and no mutarotation could be detected. The *monobromo*-derivative, $CN\cdot CHBr\,CO_2\cdot C_{10}H_{19}$, crystallises in long needles, and melts at 134–135°.

Menthyl p-tolylazocyanoacetate,—

$$C_6H_4Me\cdot N_2\cdot CH(CN)\,CO_2\cdot C_{10}H_{19},$$

crystallises in large, transparent, yellow plates melting at 93–95°; it has $[\alpha]_D = -53{\cdot}7$ in benzene, and does not exhibit mutarotation.

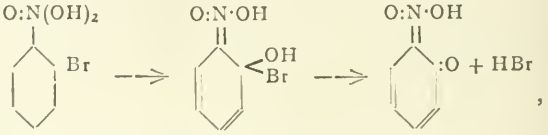
Menthyl p-bromophenylazocyanoacetate,—

$$C_6H_4Br\cdot N_2\cdot CH(CN)\,CO_2\cdot C_{10}H_{19},$$

has been obtained in two forms, one crystallising in transparent plates melting at 97–98°, and the other in slender needles having a somewhat indefinite melting-point.

17. "*The Influence of Nitro-groups on the Reactivity of Halogen Derivatives of Benzene.*" By A. Lapworth.

Four years ago, the reactivity of the halogen atoms in the *ortho*- and *para*-halogenated nitrobenzenes was discussed on the assumption that an addition product, formed by adding the elements of water or another agent to the nitro-group, underwent change in the following way :—



this reaction being impossible when the halogen is in the *meta*-position (Lapworth and Mills, *Proc.*, 1898, xiv., 159).

This explanation, which was put forward at a time when the part played by quinonoid intermediate compounds in conditioning analogous changes was not generally recognised, is revived because other reactions of this type are now being explained on similar lines.

Ordinary Meeting, Thursday, February 5th, 1903.

Dr. E. Divers, F.R.S., Vice-President, in the Chair.

Mr. W. Carter-White was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Arthur William Eastwood, B.A., Newton College, S. Devon; John Percy Edgerton, 39, White Hart Lane, Barnes, S.W.; George Howsam, School of Science, Peterborough; Alfred Owen Jones, 18, Queen's Gardens, Tetherdown, Muswell Hill; James Stewart Keir, The Grove, Ladywood Road, Birmingham; George Siddle, Middleton-One-Row, R.S.O.; William Francis John Wood, B.Sc., Doncaster Road, Barnsley; Edward Chancey Worden, Millburn, New Jersey, U.S.A.

Of the following papers, those marked * were read :—

*18. "*The Solubilities and Transition points of Lithium Nitrate and its Hydrates.*" By F. G. Donnan and B. C. Burt.

Lithium nitrate was found to yield two hydrates, $LiNO_3{,}3H_2O$ and $LiNO_3{,}\frac{1}{2}H_2O$. Of these the former has been obtained previously by Dott, who showed it to be the trihydrate and not $LiNO_3{,}2\frac{1}{2}H_2O$ as stated by Kremers and by Troost. Determinations of the solubility of these hydrates, and also of the anhydrous salt, were carried out, and in this way the various quadruple points of the system located, the position of these points being also confirmed by thermometric and dilatometric measurements. The trihydrate is of special interest as it possesses a stable melting-point. The equilibrium curve in the neighbourhood of this point was fully investigated.

The following is a list of the melting-points and quadruple points of the system :—

Cryohydrate point of $LiNO_3{,}3H_2O$, $-17{\cdot}8°$.

Melting-point of $LiNO_3{,}3H_2O$, 29·88°.

Transition point, trihydrate + semihydrate $\rightleftarrows$ saturated solution, 29·6°.

Transition point, semihydrate $\rightleftarrows$ anhydrous salt + saturated solution, 61·1°.

*19. "*The Synthesis of αα Diglutaric Acid.*" By O. Silberrad and T. H. Easterfield.

The action of iodine on the sodium derivative of ethyl α-carboxyglutarate does not lead to the formation of the hexa-ethyl ester,—

$$CO_2Et\cdot CH_2\cdot CH_2\cdot C(CO_2Et)_2\cdot C(CO_2Et)_2\cdot CH_2\cdot CH_2\cdot CO_2Et,$$

from which αα-diglutaric acid could be obtained by successive hydrolysis and loss of carbon dioxide, but gives rise to the hitherto unknown *ethyl α-iodo-α-carboxyglutarate* (*ethyl α-iodobutane-aaγ-tricarboxylate*), the reaction taking place in accordance with the following equation :—

$$CO_2Et\cdot CH_2\cdot CH_2\cdot CNa(CO_2Et)_2 + I_2 = CO_2Et\cdot CH_2\cdot CH_2\cdot CI(CO_2Et)_2 + NaI.$$

Bromine behaves similarly, yielding *ethyl α-bromo-α-carboxyglutarate* (*ethyl α bromobutane-aaγ-tricarboxylate*) (sp. gr. 1·325 at 15°/4°).

Again, on heating the sodium derivative with these halogenated esters, no condensation occurred, but instead a mixture of alkyl carboxyglutarate and a new ethyl carboxyglutaconate (b. p. 173—176°) under 15 m.m. pressure) was produced, the latter differing from its isomeride (ethyl *iso*aconitate) in that it does not contain a mobile hydrogen atom, and can therefore neither assume the enolic form nor yield a sodium derivative.

As the preceding method failed to give rise to the desired ester, its synthesis was next tried by one of the authors (O. S.) in the manner represented by the following equation :—

$$\begin{array}{l} CO_2Et\cdot CH_2\cdot CH_2I \quad NaC(CO_2Et)_2 \\ \qquad\qquad + \quad | \quad = \\ CO_2Et\cdot CH_2\cdot CH_2I \quad NaC(CO_2Et)_2 \end{array}$$

$$= 2NaI + \begin{array}{l} CO_2Et\cdot C_2H_4\cdot C(CO_2Et)_2 \\ \quad | \\ CO_2Et\cdot C_2H_4\cdot C(CO_2Et)_2 \end{array}.$$

This process proved successful, and yielded ethyl αα-di-α-carboxyglutarate (isolated as αα-diglutaric acid) together with ethyl $\Delta^{\alpha\beta}$-α-di-hydromuconate (?), ethylbutane-$\alpha\gamma\gamma\delta\delta$-pentacarboxylate (b. p. 215—218°) under 17 m.m. pressure), which, on saponification, yielded butane-$\alpha\gamma\delta$-tricarboxylic acid (m. p. 122°), and ethyl ethylenetetracarboxylate.

A fractionator was described for distilling under greatly diminished pressure; this apparatus was designed in order to overcome the difficulty due to the variation of pressure caused by throttling, which is experienced under these conditions when the ordinary columns are employed.

*20. "*Distillation of Chlorine Water.*" By A. Richardson.

Pickering (*Trans.*, 1870, xxxvii., 139) has shown that, when aqueous solutions of chlorine are heated in an open vessel, a residue containing hydrochloric acid remains behind after all the active chlorine has been expelled, and the present work was undertaken in order to find out whether the escaping chlorine was present wholly in a free state or mixed with one of its oxy-acids.

When chlorine water was heated in a retort, the distillate, which was obtained below 100°, contained free chlorine, the gas being readily displaced by a current of air; the solution in the retort, however, still contained active chlorine, for it liberated iodine from potassium iodide, bleached indigo solution immediately, and gave, on shaking with mercury, a brownish-yellow deposit resembling that obtained with hypochlorous acid. This result proved to be independent of the action of light, and was not influenced by further purification of the chlorine.

Quantitative estimations of the chlorine in the aspirated distillate gave, for the active chlorine estimated iodometrically, values double those obtained for the total chlorine found with silver nitrate after treatment with sulphur dioxide. These results show that the active chlorine is present as hypochlorous acid.

Distillation of chlorine water in a current of chlorine gas showed that the hydrochloric acid formed in the residual solution was equivalent to the hypochlorous acid found in the distillate, indicating that a portion of the chlorine reacts with the water according to the equation $Cl_2 + H_2O = HCl + HClO$.

Again, when aliquot parts of the distillate and residue obtained on distilling chlorine water were mixed, a solution having all the properties of the original chlorine water was reproduced. It would appear, therefore, that hydrochloric and hypochlorous acids are separated during distillation as the products of the partial change of chlorine water.

When chlorine water was heated in a flask provided with a reflux condenser, so that the distillate returned to the original solution, the ratio of active to total chlorine found was that required for a solution of free chlorine, showing that the solution is stable when the separation of the two acids is prevented.

A further study of the change showed that the amount of hypochlorous acid passing over decreased with the increase in strength of the hydrochloric acid formed in the solution. With very dilute solutions of chlorine water, the whole of the free halogen employed entered into reaction with the solvent, the oxy-acid only having been found in the distillate.

Finally, distillation of very dilute chlorine water in a vacuum at the ordinary temperature gave a distillate containing the oxy-acid, showing that the reaction occurs at the ordinary temperature as well as at the boiling-point.

21. "*A New Vapour Density Apparatus.*" By John S. Lumsden.

This apparatus is based on the principle that the molecular weights of all substances in the state of gas, when occupying the same volume and at the same temperature, exert the same pressure. The pressure produced at a given temperature by the molecular weight in milligrms. is either found experimentally by vaporising a substance of known molecular weight or calculated from the dimensions of the apparatus; then, from the pressure produced by vaporising a weighed quantity of the substance the molecular weight of which is required, the weight in milligrms. which would produce the milligrm. molecular pressure is found. This is taken as the molecular weight.

No barometric reading is necessary, and when the constant of the apparatus has been found and the substance weighed, the experiment is completed in two minutes, and the calculation of the result may be made in another two minutes.

By slightly modifying the arrangement of the apparatus, the substance may be vaporised under diminished pressure or in an inert gas, and the experiment may be performed at any temperature. The instrument, which is quite as accurate as the Victor Meyer apparatus, is, owing to its simplicity, well adapted for general laboratory work.

22. "*A New Form of Pyrometer.*" By John S. Lumsden.

A constant volume instrument was described in which a weighed quantity of a substance is vaporised and the pressure measured by a mercury gauge.

The pressures produced by equal weights of substance are proportional to the absolute temperatures; therefore, if at two temperatures the pressures produced by equal weights are measured and one temperature is known, the other can be calculated.

The instrument may be made of glass, porcelain, or metal, and high temperatures may be measured within a few degrees.

23. "*Tertiary Butylphenol.*" By E. W. Lewis.

The author draws attention to the non-formation of phenyl-*ter.*-butyl ether on digesting phenol in alcoholic solution with *ter.*-butylchloride and excess of alkali, and to the production in these circumstances of the isomeric *ter.*-butylphenol. Other instances of the difficulty attending the preparation of phenol ethers containing a tertiary radicle in place of the hydrogen of the phenolic hydroxyl group are cited in the paper.

Anniversary Dinner.

It has been decided by the Council to arrange for a Dinner of the Fellows of the Society and their friends on Wednesday, March 25th, 1903, this being the day fixed for the Annual General Meeting. Further particulars will be announced shortly.

ROYAL SOCIETY OF NEW SOUTH WALES.

The General Monthly Meeting of the Society was held at the Society's House, No. 5, Elizabeth Street North, on Wednesday evening, December 3, 1902; Prof. Warren, M.Inst.C.E., Wh.Sc., President, in the Chair.

The following paper was read:—

"*On the presence of Platinum and Iridium Metals in Meteorites.*" By Professor Liversidge, LL.D., F.R.S.

At the September meeting of the Society the author described the occurrence of gold in meteorites. In certain cases the gold is accompanied by one or more of the platinum and iridium metals. The Boogaldi meteorite contains both gold and one or more of the platinum metals; these metals do not appear to be uniformly diffused through the meteorite, for some parts apparently contain a much larger proportion than others. The meteoric iron was dissolved in hydrochloric acid, the usual black carbonaceous residue was then ignited and afterwards ground in an agate mortar. On washing off the lighter powder the metals are seen as lustrous yellow and silvery spangles; by means of a needle these can for the most part be picked up and separated. The first few white metallic spangles obtained were insoluble in a mixture of nitric and hydrochloric acids when warmed and evaporated to dryness on a microscope slide (the tests were at first applied under the microscope), and it looked as if the white spangles consisted solely of iridium metals insoluble in nitro-hydrochloric acid, but afterwards it was found that another portion of the meteorite yielded a larger quantity of them, and this —treated with a larger volume of aqua regia—dissolved. Both gold and platinum were separated from the solution by the usual wet methods; iridium and other metals of this group are probably present. The amount of the platinum metals in the Boogaldi meteorite is comparatively large, being at the rate of several ounces per ton; details will be found in the paper.

The Action of Bromacetic Ether on Nitrite of Silver.—Roland Scholl and Alwin Schofer.—The authors have carried out this reaction on a large quantity of matter (1275 grms. of bromacetic ether and 1815 grms. of nitrite of silver) so as to be able to isolate all the products. They were not able to obtain any nitroacetate of ethyl, but they were enabled to characterise the following products:—Glycolate of ethyl, ethyl-glycolate of ethyl, nitrate and nitrite of glycolic ether, oxalate of ethyl, anhydronitroacetate of ethyl, bisanhydronitroacetate of ethyl, and, finally, a compound with the formula $C_{12}H_{15}NO_8$. The three last products are new. *Anhydronitroacetate of ethyl*, $CO_2C_2H_3{-}C{\equiv}N{=}O$, crystallises from boiling benzene in colourless needles fusible at 111—111·5°, soluble in acetic acid, ether, and chloroform, slightly soluble in water and alcohol, almost insoluble in cold C_6H_6,CS_2 and ligroin. The bisanhydronitroacetate of ethyl, $\begin{matrix} CO_2C_2H_5{-}C{=}N{=}O \\ | \quad | \\ O{=}N{=}C{-}CO_2C_2H_5 \end{matrix}$, is an oil with a slight odour, boiling at 160° under 11 m.m., and at 233—234° at the ordinary pressure, with slight decomposition; the reduction of this ether results in glycocol; the potassium salt of the corresponding acid crystallises with $3H_2O$; when treated with HCl it gives the free acid in needles, fairly soluble in water and alcohol, slightly soluble in ether; it is very unstable and explosive. The amide decomposes at 120—121°, the methylamide fuses at 162°, the benzylamide at 174—175°, the allylamide at 95—97°, the diethylamide decomposes at 167°. The compound $C_{12}H_{15}NO_8$ is a yellowish oil boiling at 188—190° under 11 m.m.; it is probably the ether of a tricarbonic acid, $C_3O_2N(CO_2H)_3$; with ammonia it gives a white powder which should be the corresponding triamide; the figures of the analysis of this latter body do not agree very well with theory.—*Berichte*, vol. xxxiv., p. 870.

NOTICES OF BOOKS.

General Index to the First Twenty Volumes of the Journal of the American Chemical Society, 1877-1898. Easton, Pennsylvania. 1902. Pp. 237. 8vo.

This valuable contribution to chemical bibliography has been prepared under the supervision of two gentlemen who modestly sign only their initials to the explanatory preface, but who are recognised thereby as Professors Edward W. Morley and Olin F. Tower, both of Adelbert College, Cleveland, Ohio. The volume comprises an author and a subject-index, besides indexes to new books reviewed in the journal, and to obituaries. The whole seems to be carefully prepared, the original cards having been twice verified; few liberties have been taken with titles except in spelling uniformly certain words. The work includes not only the "Journal" of the Society, but the earlier publication known as "Proceedings," issued in two volumes in 1877-79.

The thanks of all chemists, as well as of librarians, are due for this laborious undertaking, which has been a labour of love on the part of the gentlemen named.

Twelfth Census of the United States. Manufactures, Chemicals and Allied Products. Census Bulletin, No. 210, Washington, D.C. 1902. Pp. 306. 4to.

The subject of chemicals and their manufacture was included in the tenth census, and also in the eleventh, but the attempts made in those years bear little resemblance to the thorough, comprehensive, and well arranged matter in the volume under review. The government officials in charge of the twelfth census were fortunate enough to secure the services of a most able chemist to take the direction of the arduous task, Professor Charles E. Munroe, Ph.D., of the Columbian University, Washington, D.C., and a Past President of the American Chemical Society, who is known as authority on high explosives. Associated with him was the painstaking, indefatigible Dr. Thomas M. Chatard.

Their voluminous report gives statistics, in several distinct tables, of fertilisers, dye-stuffs and tanning materials, paints, varnishes, explosives, essential oils, chemicals, bone, ivory, and lamp-black, all arranged by States; preceding these tables is an admirable summary of the growth of chemical industry in the United States This summary shows wide reading and intelligent compilation, with short bibliographies at the end of each section. The number of active establishments reported is 1827; owing to the hearty co-operation of the managers of these works the statistics and information have been made unusually full and accurate.

In an appendix of 146 pages is given a digest of United States patents, arranged under nineteen heads, and of great value to inventors. Each item contains the number and date of the patent, the name of the claimant, and a synopsis of the claim.

The chief statistician for manufactures, S. N. D. North, in transmitting Professor Munroe's report to the Director of the Census, characterises it as "exhaustive and valuable," and adds:—"Nothing approaching it in any particular has ever before been presented at any census of the United States."

The voluminous Bulletin lacks a table of contents, and of course an index under the circumstances cannot be expected; nevertheless, it will long be an authoritative and satisfactory source of information on the subject of chemical manufactures in the United States at the close of the nineteenth century. H.C.B.

A Course in Botany and Pharmacognosy. By Henry Kraemer, Ph.B., Ph.D. Illustrated with Plates from Original Drawings by the Author. Philadelphia: Press of Edward Stern and Co. 1902. Pp. 384.

The material used in compiling this volume has been furnished largely by medicinal plants and the commercial

vegetable drugs. Although certain mineral drugs are used largely, there can be no doubt that vegetable remedies are the more natural ones, and are far better suited to mankind, as a rule, than such materials as calomel, sulphate of magnesia, arsenic, &c.

The subject of morphology has been more or less extensively treated by the author, particularly that of the plant cell, because this knowledge is of fundamental importance in the study of vegetable drugs.

The book is divided into four parts, on plant morphology, pharmacognosy, reagents, and illustrations respectively.

Part I. consists of two chapters; the first is on the cell, and deals with cell-contents, both organised, such as protoplasm, plastids, &c., and unorganised, like starch, sugars, alkaloids, mucilages, oils, and colouring principles. The origin and composition of cell-walls, and the forms of cells are described in Sections D and E of this chapter. Chapter II. is on the vegetative and re-productive parts of the plant, the vegetative section dealing with the roots, stem, and leaves, while Section B is devoted to the flower and its functions.

Part II., on Pharmacognosy, is divided into two chapters, viz., Chapter 1, "Crude Vegetable Drugs," and Chapter 2, "Powdered Vegetable Drugs"; this part fills the bulk of the book, covering 213 pages. Pharmacognosy means a knowledge of drugs, and it is usually limited to the study of drugs of a vegetable origin; in these pages a large number of drugs are described *seriatim*, their constituents, appearance, allied plants, and probable adulterants being given in most cases.

On page 266 and following, there is a key for the study of powdered drugs, which will be found of great assistance; in the remaining portion of the chapter each of these powders is dealt with specifically at greater length. There are seventeen plates of illustrations which merit close attention, and a good index of 52 columns.

Subject-list of Works on General Science, Physics, Sound, Music, Light, Microscopy, and Philosophical Instruments in the Library of the Patent Office. London: Darling and Son, Ltd., and the Patent Office. 1903. Pp. 183.

This subject-list, No. 11 of the Patent Office Series, consists of two parts:—(*a*) A general alphabet of subject headings, with entries in chronological order of the works arranged under these headings; (*b*) a key or summary of these headings shown in class order.

It is recommended that these lists be used strictly as subject guides and not for the purpose of tracing a work by its title, as the contents of the work have been considered in making an entry in preference to the language of the title-page, which is often misleading.

The present list comprises 1849 works, representing 9281 volumes; the catalogue entries relating to these works number 2069, and are distributed under 196 headings and sub-headings.

A History of Hindu Chemistry; from the Earliest Times to the Middle of the Sixteenth Century, A.D.; with Sanskrit Texts, Variants, Translation, and Illustrations. By Praphulla Chandra Ray, D.Sc., Professor of Chemistry, Presidency College, Calcutta. Vol. I. London: Williams and Norgate. 1902. Pp. 217.

Chemistry among the ancients has always been closely allied with medicine, metallurgy, and the transmutation of metals. In India, more than in Europe, chemistry has been evolved principally in connection with medicine, but it was always backed up, so to speak, with an appeal to the gods, and the higher gods of the *Rigveda* are almost entirely personifications of the elements and the other natural phenomena, such as fire, wind, the sun, and the dawn.

The earliest literary record of Indian medicine, the "*Atharva-veda*," deals chiefly with sorcery, witchcraft, and demonology. In the "*Ayurvedic*" period the Hindu system of medicine was arranged on a rational basis, with a scientific terminology; the two great works of this period are the "Charaka" and the "Susruta," in which the subject is found to have made a distinct advance. Then followed the "transitional" period, the "Iantric period," and the "Tatro-chemical" period.

The first or "Ayurvedic" period was from the pre-Buddhistic Era to about 800 A.D.; the transitional period is from 800 A.D. to about 1100 A.D.; while the last two are from 1100 to 1300 A.D. and 1300 to 1550 A.D. respectively.

The book is of interest, inasmuch as it shows the considerable amount of knowledge possessed by the Hindus. Their knowledge was principally rule-of-thumb work, which gave them very fair practical results.

Elektromagnetische Aufbereitung ("Electromagnetic Dressing"). By F. Langguth. Halle-a-S.: Wilhelm Knapp. 1903.

This volume forms a part of the new "Handbuch der Elektrochemie," the issue of which has recently commenced, and is complete in itself, the subject treated of being capable of being comprised in one moderate sized volume. The principle of electromagnetic dressing of ores is explained, and the most important kinds of ore-separations are described with considerable attention to detail, the latest developments in this respect being as far as possible included. Valuable statistics dealing with the results of the various magnetic separation processes conclude the volume, which gives an adequate account of the essentials of the subject.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 4, January 26, 1903.

Researches on the Alkaloids of Quinquina: Cinchonine, Cinchonidine, and Cinchonamine.—MM. Berthelot and Gaudechon.—The authors continue their researches on the alkaloids of quinquina, and find the thermal constants of cinchonine, cinchonidine, and cinchonamine.

Nickel Steel.—Léon Guillet.—The addition of nickel to steel lowers the magnetic transformation point of the steel. The author examines with a microscope three series of very pure steels containing only traces of phosphorus, silicon, sulphur, and manganese. He finds that until the steel contains 7 per cent of nickel the structure is identical with that of ordinary steel containing carbon. When, however, the proportion of nickel attains 10 per cent, the micro-structure changes completely, white crystals appear on the surface; and when 25 per cent of nickel is present, these crystals are very numerous.

The Existence of Electrolytic Superoxides of Lead, Nickel, and Bismuth.—A. Hollard.—It has always been admitted that the lead peroxide which is deposited at the anode of a saline lead solution through which a current passes is lead dioxide, PbO_2. Contrary to this assertion, the author finds—(1) That the analytic factor, 0·866, is too great, and that, in addition to the dioxide PbO_2, higher oxides are deposited at the anode; (2) that the proportion of these higher oxides is greater as the concentration of the lead in the bath is decreased. Nickel and bismuth also form similar oxides when their solutions are subjected to electrolysis.

Equilibrium produced between Copper, Silicon, and Manganese. Manganese Silicide, Si_2Mn.—P. Lebeau.—An investigation of the action of a great number of metals on copper silicide leads the author to the conclusion that certain of them, such as silver, tin, zinc, and aluminium, have a real affinity for copper, forming an alloy with this metal, and causing the silicon to crystallise out. Other metals, on the contrary, react on molten copper silicide, uniting with the silicon to form a definite silicide, and giving at the same time compounds with silicon and copper. To investigate the equilibrium of these systems, the author prepares a series of metallic masses containing copper, silicon, and another metal in definite proportions. The experiments led to the preparation of three definite silicides of manganese—$SiMn_2$, SiMn, and Si_2Mn.

Two Phosphorus Acids derived from Methylethyl ketone.—C. Marie.—Methylethylketone when acted upon by H_3PO_2 does not give the diketonic acid corresponding to dioxyisopropylhypophosphorous acid. The monoketonic acid, $PO_2H_3CH_3COC_2H_5$, is obtained, and, by oxidation, the oxyphosphinic acid, $PO_3H_3CH_3COC_2H_5$. These two acids constitute the superior homologues of the oxyisopropylhyperphosphorous and oxyisopropylphosphinic acids, which the author has already described.

A New Di-iodated Phenol.—P. Brenans.—In a previous research the author investigated the di-iodated derivatives of phenol, $OH-C_6H_3-I_2$-(1.2.4), (1.2.6), and (1.3.6). He now discusses a fourth isomer, di-iodated phenol, $OH-C_6H_3-I_2$-(1.3.5), which he obtains from di-iodated orthonitraniline, $C_6H_2-NH_2-NO_2-I_2$-(1.2.4.6), by the following succession of reactions:—(1) The diazoic derivative of the latter substance, when decomposed by absolute alcohol, gives the di-iodated nitrobenzene, $C_6H_3-NO_2-I_2$ (1.3.5); (2) the base resulting from the reduction of this nitro-di-iodo benzene, di-iodated aniline, $C_6H_3-NH_2-I_2$-(1.3.5), is subjected to diazotisation; and (3) finally, the diazoic salt, when heated in the presence of water, gives di-iodophenol, $OH-C_6H_3-I_2$-(1.3.5).

Rotatory Power in the Homologous Ethers of Borneol, Isoborneol, and Camphocarbonic Acid.—J. Minguin and G. de Bollemont.—The rotatory power of the bornylic ethers is measured in the case of bornyl stearate, oleate, crotonate, and cinnamate. Also that of the isobornylic ethers, isobornyl formate, acetate, propionate, isobutyrate, butyrate, valerianate, laurate, and the camphocarbonic ethers, camphocarbonate of methyl, ethyl, propyl, isobutyl, and allyl.

Chloruration of Substituted Aromatic Carbides by Ammoniacal Lead Chloride.—A. Seyewetz and P. Trawitz.—Monochlorated benzene is only very slowly attacked at boiling-point or in sealed tubes at about 210°, when acted upon by plumbo-ammoniacal chloride. Bromated and iodated benzene give chlorobromo- and chloroiodo-derivatives. With the homologues of benzene already chlorated in the aromatic radicle, there is no new substitution in this radicle, but only in the lateral chain. In the aromatic carbides having a lateral chain, substitution only takes place in this chain by a halogen; the substitution continues without the aromatic radicle being attacked. The presence of nitrated groups hinders chloruration by plumbo-ammoniacal chloride.

Researches on $\alpha\beta$-Dimethylglutaric Acids.—E. E. Blaise.—The author's researches on the $\alpha\beta$ dimethylglutaric acids show that the acid, $C_7H_{12}O_4$, obtained from ethyl bromopivalate, is different from one at least of the predicted $\alpha\beta$ dimethylglutaric acids.

Preparation and Properties of Hexanediol 1.6, or Hexamethylenic Glycol and its principal Derivatives.—J. Hamonet.—In preparing hexamethylenic glycol, the author first transforms diphenoxyhexane into the di-iodated hexane, then into diacetone, and finally saponifies this latter substance.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 13.

Preparation and Properties of Sulphammonium.—H. Moissan.—Already noticed.

Some Properties of Lime at its Fusing-point.—H. Moissan.—Already noticed.

Research on the Constitution of Compounds of Chromium.—G. Wyrouboff.—The author gives a list of thirty-one double oxalates recently obtained by him. Of these thirty-one compounds, twelve are aluminoxalates, nine are chromoxalates, and the remaining ten are ferrioxalates. The question arises—What is the exact nature of these bodies? All that is known for certain is that they are abnormal or "complex," as their elements cannot be detected in their ordinary reagents, and they do not contain water of constitution. With a view to elucidating this problem, the author has made a number of experiments with oxalate of chromium, $Cr_2O_3,3C_2O_3,25H_2O$. The first fact learnt is that oxalate of chromium, produced under particular conditions, is a crystallisable salt, comparable with all the violet salts of chromium; it is unstable, and is transformed by dehydration into another violet compound which is uncrystallisable. The second fact is that the violet sulphate of chromium can be transformed, under certain conditions, exactly the opposite to the last salt, into an abnormal compound, while still retaining its violet colour.

Crystallographic Constants of the Bromised Derivatives of Benzylidene-camphor and Benzylcamphor.—J. Minguin.—A number of crystallographic observations of the above derivatives are given, but it is remarked that in no cases have hemihedric facets been observed, although the internal structure of the crystals is dissymmetric.

Crystallographic Determination of Methylcamphocarbonate of Methyl and Methylcamphocarbonate of Ethyl, of the Methylic Ether of the Camphoric Mononitrite, and of its Isomer, Methylcamphorimide.—J. Minguin.—Methylcamphorimide is distinguished by its crystallographic characteristics from the methylic ether of the camphoric mononitrite.

Contribution to the Study of the Borneols and their Ethers. Their Crystallographic Examination. The Crystallographic Examination of the Bornylates of Chloral and of Bromal.—J. Minguin.—A long paper, unsuitable for abstraction.

Some Derivatives of the Thio-cresols.—Ch. Rabaut.—The para-thio-cresols were obtained from sulphocyanate of paracresyl, $C_8H_7NS=CH_3^{(1)}.C_6H_4^{(4)}.SCH$, which, in its turn, was prepared from paratoluidine by Sandmeyer's reaction. The sulphocyanate of paracresyl, treated with an alcoholic solution of sulphydrate of potassium, or by zinc and hydrochloric acid, gives thio-paracresol. With acetate of lead, thio-paracresol gives a precipitate, yellow when cold and red when heated. This precipitate can be transformed very easily. By dry distillation it gives $PbS+(CH_3C_6H_4)_2S$; when treated with bromine in acetic solution, we obtain $(CH_3C_6H_4)_2S_2$; with chloride of acetyl, it gives the acetic ether of thio paracresol. A mixture of equal molecules of sulphocyanate of paracresyl and monochloracetic acid, heated to boiling, gives off large quantities of hydrochloric acid, and, on cooling, gives a black mass slightly soluble in water. Treated with a dilute boiling solution of soda, and, when cool, with hydrochloric acid, this mass gives a crystalline precipitate, $C_9H_{10}O_2S$.

Production of Sulphuretted Hydrogen during Alcoholic Fermentation.—M. and E. Pozzi Escot.—(See p. 87).

The Basic Products of the Hydrolysis of Muscle.—M. Etard.—It is proved that, by hydrolysis, alimentary flesh gives a large quantity of alkaloids; it is not to be doubted that digestive hydrolysis does the same, the more

so that if they are of a diastasic nature, they are also microbic.

The Solubility of Prussian-blue under certain conditions.—Ch. Coffignier.—The presence of alcohols of the fatty series greatly facilitates the solvent action of hydrochloric acid. The author gives the results obtained with the principal alcohols, using hot mixtures of equal volumes of hydrochloric acid and the alcohol. Ethylic alcohol gives a solution which soon deposits the prussian-blue, but the other alcohols give solutions which could be kept for several weeks without alteration.

The Order in which the Usual Manipulations should be made in the Diagnostic Analysis of Urines.—Henri Taffe.—Unsuitable for abstraction.

Detection of Salicylic Acid in Foods by the Coloured Reaction of the Ferric Salts.—Henri Taffe.—The author recommends as a solvent-extractor, a mixture of equal parts of ethylic ether and petrol ether, or better still, as the result of more recent experiments, petrol-ether alone of a density = 0·700. It has a further advantage of not dissolving hydrochloric acid easily, and as is known, free mineral acids in excess diminish the intensity of the colouration of the ferric salicylate, and consequently the sensitiveness of the test.

No. 14.

Action of Hydrochloric, Hydrobromic, and Hydrofluoric Acids on Monopersulphuric Acid.—E. Wedekind. — During the preparation of Caro's reagent, $SO_2 \begin{matrix} O-OH \\ < \\ OH \end{matrix}$, by mixing sulphuric acid with ordinary peroxide of hydrogen which contains a certain quantity of hydrochloric acid, we often observe the odour of chlorine very distinctly, which can only result from the oxidation of the hydrochloric acid. By means of M. Baeyer's dry reagent, obtained by the action of concentrated sulphuric acid on persulphate of potassium, we can oxidise hydrochloric acid in the cold, and thus obtain chlorine. A concentrated solution of hydrobromic acid behaves in a similar manner, giving off bromine fumes. With the hydracids in the gaseous state the reaction is not so violent, but it is very characteristic. Since monopersulphuric acid oxidises the hydracids, and the water formed during the reaction can be absorbed by sulphuric acid, it was natural to try the action of this reagent on hydrofluoric acid. Our experiments showed that sulphate of potash is fairly stable in contact with fluorine in the cold, but decomposes when heat is applied. One series of experiments showed us that anhydrous hydrofluoric acid is perfectly stable in the presence of monopersulphuric acid; there is no hope, therefore, of preparing fluorine by this method. If we add anhydrous hydrofluoric acid to the solid reagent in a platinum crucible no reaction takes place; after about ten minutes, gas is given off by the evaporation of the hydracid. If we pass a current of hydrofluoric acid gas through a platinum tube containing the solid reagent, the gas escaping from the tube will not inflame crystallised silicon. The author also gives other experiments showing that there is no action with hydrofluoric acid similar to that with hydrochloric and hydrobromic acids.

Ammonium Amalgam.—Henri Moissan.—Already noticed.

Research on the Constitution of Compounds of Chromium.—G. Wyrouboff.—At the end of a very long paper the author summarises his results, and draws the double conclusion, that mineral compounds very simple in appearance may have a very complicated constitution, even as complicated as that of carbon compounds; and that our simple conceptions of inorganic chemistry ought to be considerably modified, and the idea of multiple functions should be introduced, as in organic chemistry.

The Separation of Glucinum.—G. Wyrouboff.—Already inserted.

Coloured Reaction of Uranium Salts with Peroxide of Hydrogen.—J. Aloy.—Will be inserted in full.

Some Salts of Benzylamine.—René Dhommée.—Already noticed.

Some Derivatives of Anthraquinone obtained from the Aloïnes.—E. Léger.—Already noticed.

The Production of Derivatives of Anthraquinone from the Aloïnes from Natal Aloes.—E. Léger.—*Action of Binoxide of Sodium on Nataloïne and on Homonataloïne.*—This reagent does not react in the cold on either of the two aloïnes in alkaline solution. The addition of hydrochloric acid to the yellow alkaline liquid precipitates the aloïnes unchanged. The same is the case on the water-bath. 250 c.c. of water at 80—85°, then 5 grms. of nataloïne, and a few drops of soda-lye are placed in a dish on the water-bath. Then 25 grms. of Na_2O_2 are gradually added during half-an-hour. The yellow solution takes a deeper colour, and when the reaction is finished even a thin layer appears orange-yellow. It is cooled, and hydrochloric acid added, and a yellowish brown flocculent precipitate is formed. The liquid is shaken up with its own volume of ether, which takes up the product and becomes yellow. The ethereal solution is distilled to dryness. Take up with boiling methylic alcohol, and allow to crystallise. The crystals are re-dissolved in boiling methylic alcohol; we then add washed animal-black, and boil for fifteen to twenty minutes, using a reflux condenser, then filter. The solution, concentrated by distillation, gives pale orange-yellow anhydrous needles, very long and fine. Homonataloïne gives the same body; its formula is found to be $C_{16}H_{12}O_5$.

MISCELLANEOUS.

University College Chemical and Physical Society.—On Wednesdays, February 25th and March 4th, at 8.30 p.m., Dr. M. W. Travers will lecture on "The Attainment and Measurement of Low Temperatures." There will be liquid hydrogen on both days. Visitors invited.

Royal Institution.—On Tuesday next (February 24th), at 5 o'clock, Sir William Abney will deliver the first of a course of three lectures at the Royal Institution on "Recent Advances in Photographic Science"; on Thursday, at the same hour, Prof. L. C. Miall begins a course of three lectures on "Insect Contrivances"; and on Saturday (February 28th), at 3 o'clock, Lord Rayleigh delivers the first of six lectures on "Light—its Origin and Nature." The Friday Evening Discourse on February 27 will be delivered by Adolph Liebmann on "Perfumes, Natural and Artificial"; on March 6th, by Prof. J. G. McKendrick on "Studies in Experimental Phonetics"; and on March 13th, by Prof. Karl Pearson on "Character Reading from External Signs."

Cyanide Poisoning.—At a recent meeting of the Council of the Chemical and Metallurgical Society of South Africa the matter of cyanide poisoning and its treatment was brought forward and discussed, and it was unanimously decided that in view of the widespread use of the cyanide process, and the accidents and ailments which arise therefrom, it was very desirable that the Society should investigate the nature of the poisoning and examine into the various remedies, antidotes, and treatments, with a view to discovering the most efficacious procedure in cases of poisoning, and recommending the same for general adoption by the industry. In pursuance of this discussion the Council has appointed a Sub-Committee, consisting of Messrs. A. F. Crosse, E. H. Johnson, and J. Yates, to carry out the necessary investigations and to report thereon. In starting upon their labours, the Sub-Committee is of opinion that it is necessary to have compiled particulars of the fatalities which have so far occurred and also the ailments both past and

existing, together with an account of the treatments adopted, and their effect. As this information is necessary, and will be, they are convinced, of the greatest service, they trust that as much detail as possible as regards treatment, &c., will be sent to the Secretary, Frederick Rowland, Assoc.C.I.S., Box 4375, Johannesburg, Transvaal.

Action of Hypophosphorous Acid on the Diazoic Compounds.—J. Mai.—The author has observed that when hypophosphorous acid reacts on the diazoïc compounds, the latter are reduced, giving the corresponding hydrocarbide as the principal product. When, for instance, the chloride of paradiazotoluene is added to hypophosphorous acid, and the mixture left for some days at 0°, 67 per cent of the theoretical amount of toluene is found in the product of the reaction. With chloride of diazobenzene the author obtained benzene and diphenyl; 3 grms. of aniline gave him 1 grm. of benzene and 0·5 grm. of diphenyl. The reaction with chloride of tetrazodiphenyl gave 60 per cent of the theoretical amount of diphenyl, and is a good method of preparing this hydrocarbide; chloride of diazonaphthalene gave naphthalene; in some cases it is advisable to help on the reaction by careful heating.—*Berichte*, vol. xxxv., p. 162.

New Method for the Direct Volumetric and Gravimetric Estimation of Mercury, Copper, and Zinc.—R. Cohn.—Mercuric thiocyanate, $(CyS)_2Hg$, is very slightly soluble in water, but is soluble in an excess of mercuric chloride or of an alkaline thiocyanate; in dilute solution, when acidulated with nitric acid, it does not colour ferric salts. We can estimate the mercury exactly in a solution of $HgCl_2$, for example, by adding first a little nitric acid and iron-alum, then a measured excess of a decinormal solution of $CySNH_4$; then we pour in a decinormal solution of nitrate of silver so as to pass the decolouration-point, and then add more thiocyanate until the brown colouration reappears and remains for some minutes. In an analogous manner we can estimate copper or zinc volumetrically, as these metals form double mercuric thiocyanates, $(CyS)_2Hg.(CyS)_2M$. To the solution under examination we add a known quantity of a solution of $HgCl_2$ and of $CySNH_4$. But in these latter cases we can also proceed gravimetrically by collecting and roasting the precipitate of the double thiocyanate.—*Berichte*, vol. xxxiv., p. 3502.

Direct Gravimetric Estimation of Boric Acid.—A. Partheil and J. A. Rose.—Boric acid is insoluble in anhydrous ether at the ordinary temperature, but it is slightly soluble in ether saturated with water (0·188 grm. in 100). On the other hand, it is not at all volatile in dry vacuo at the ordinary temperature, neither is it carried over by ether vapour. Hence, we get a method for its estimation by exhaustion with ether, something like the estimation of a fatty body. The apparatus used for the exhaustion by "perforation," consists of a tared matras into which 20—30 c.c. of ether is poured: this vessel communicates with a vertical condenser by means of a straight tube and a serpentine. In this latter we place the solution in which we wish to estimate the boric acid (for example, a borate with dilute hydrochloric acid), and the tubes are arranged in such a manner that the ether falling back from the condenser goes to the bottom of the serpentine tube, ascends this latter throughout its whole length while traversing the column of boriferous liquid, and finally discharges into the distilling flask without carrying with it any of the aqueous solution. The ether is kept boiling briskly for eighteen hours; the whole of the BoO_3H_3 having passed into the flask by this time, nothing remains but to detach the latter, allow the ether to evaporate off in a sulphuric acid desiccator, and weigh; the difference in weight gives the boric acid. It is important that the solution under examination should not contain sulphuric, nitric, phosphoric, or arsenious acids, nor notable quantities of Fe_2Cl_6 or $ZnCl_2$.—*Berichte*, vol. xxxiv., p. 3611.

Superphosphate as a Top-dressing for Grass Lands.—The total area under crops in the United Kingdom is over 47¾ million acres, and of this acreage nearly 28½ millions, or more than one-half, is returned as permanent pasture. It is admitted that much of this vast area of grass is stunted and starved, for the farm-yard manure produced is totally inadequate to fertilise even a portion of it. The great necessity for improving grass lands has occupied the attention of agricultural colleges and county councils during the past three years, and hundreds of experiments, conducted all over the United Kingdom, have demonstrated the fact that an application of 4 or 5 cwts. of superphosphate per acre not only increases the yield, but immensely improves the quality, with more after-grass and the suppression of moss. Many farmers have been working in the same direction, combining practice with science, and the Chemical Manure Manufacturers' Association have just issued a pamphlet comprising a selection from the numerous reports received. A perusal of them will be sufficient to convince anyone that the improvement of our pastures is a matter of prime importance, and that this can be effected at a low cost, either by superphosphate alone, when phosphates alone are deficient in the soil, or by a compound manure containing soluble phosphates, ammonia, and potash.

The Speed of Decomposition of Nitrite of Ammonium.—K. Arndt.—The author has examined the speed with which nitrogen is given off from solutions of nitrite of ammonium for temperatures comprised between 60° and 70°, and concentrations between 0·3 and 0·6 molecules per litre. This speed is tripled by an elevation of temperature of 10°. The non-dissociated portion of the nitrite of ammonium is split up into nitrogen and water under the influence of free nitrous acid. An addition of sulphate of ammonium accelerates the speed of the reaction, as it diminishes the electrolytic dissociation of the nitrite. Nitrite of sodium also prevents dissociation, and notably increases the concentration of the free nitrous acid. Salts which contain neither ammonium nor nitrous acid, on the contrary, diminish the speed of the reaction; the most active, from this point of view, are the salts of potassium; next, those of sodium, then those of magnesium; the sulphates are more active than the nitrates and the chlorides. This diminution of speed arises as much from the diminution of concentration of the ammonium nitrite as from the diminution of concentration of the free nitrous acid. The speed is diminished greatly by very small quantities of ammonia, and increased considerably by very small quantities of acid. Experiments show that in a solution of nitrite of ammonium at 0·6 molecule per litre, one-half per cent is split up into acid and base at 75°, and one-quarter per cent at 70°.—*Zeit. Physik. Ch.*, vol. xxxix., p. 64.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Society of Arts, 8. (Cantor Lectures). "Paper Manufacture," by Julius Hübner.

TUESDAY, 24th.—Royal Institution, 5. "Recent Advances in Photographic Science," by Sir William Abney, K.C.B., D.C.L., F.R.S.

WEDNESDAY, 25th.—Society of Arts, 8. "Tonkin, Yunnan, and Burma," by Fred. W. Carey.

THURSDAY, 26th.—Royal Institution, 5. "Insect Contrivances," by Prof. L. C. Miall, F.R.S.

—— Society of Arts, 4.30. "Gleanings from the Indian Census," by Jervoise Athelstane Baines, C.S.I.

FRIDAY, 27th.—Royal Institution, 9. "Perfumes, Natural and Artificial," by Adolph Liebmann, M.A., Ph.D.

—— Physical, 5. "On the Measurement of Small Capacities and Inductances," by Prof. Fleming and Mr. Clinton. "On the Interpretation of Milne Seismograms," by Dr. Farr. "On the Thickness of the Liquid Film formed by Condensation at the Surface of a Solid," by Dr. Parks.

SATURDAY, 28th.—Royal Institution, 3. "Light—its Origin and Nature," by Lord Rayleigh, F.R.S., &c.

THE CHEMICAL NEWS.

Vol. LXXXVII., No. 2257.

ON THE "EMANATION SUBSTANCE"* FROM PITCHBLENDE, AND ON RADIUM.

By F. GIESEL.

The radio-activity of the compounds of thorium and their characteristic emanation has been very thoroughly investigated by Rutherford (*c.f.* E. Rutherford and Soddy, *Zeit. für Physikal. Chem.*, 1902, xlii., 81). His endeavours to prove that the relatively very insignificant activity of thorium is due to the presence in very small quantity of a strongly active substance were unsuccessful. It is true that Rutherford, by extraction of thorium hydroxide with water or by precipitation of thorium salts with ammonia, obtained, after evaporation or expulsion of the ammonia respectively, small residues almost free from thorium, which were considerably more active than the thorium used, but the properties of these residues were altered. While the thorium by such treatment had lost a part of its activity, after some time it regained its original activity, but, on the contrary, the extracted substance, which Rutherford called "ThX," gradually decreased in activity up to the amount of the thorium present,†

Hence Rutherford concluded that the thorium itself must be the primarily active substance, and that "ThX" is formed from it continually by re-arrangement of the atoms.

Now, I have obtained a body from pitchblende (*Berichte*, 1902, xxxv., 3610), which, firstly, possesses to a considerably higher degree the same kind of activity as thorium, and secondly, unlike "ThX," has not diminished at all in linear radiation and emanation in about six months. But as the physical properties agree in other respects, and as it also appears to be related to thorium (and the rare earths), from these two new facts mentioned above we are led to adopt a different view from Rutherford's concerning the origin of the activity of thorium.

The emanation substance of pitchblende belongs to the group of cerium earths, or at any rate reacts in the same way. I have already shown (*Berichte*, 1902, xxxv., 3611) that the rare earths obtainable from pitchblende possess a constant activity. I was not then able to observe an emanation‡ because this, as has already been shown, does not belong equally to all compounds, but is dependent upon chemical conditions.

The method of preparation of the raw material for the emanation substance is the same as that employed for the separation of the rare earths, and is best effected by means of potassium sulphate, after removal of the heavy metals. Hydrogen peroxide gives with the solution of the potassium double salt a fairly active precipitate, displaying the emanation. The precipitate with oxalic acid, which also contains the emanation substance, and in consequence of the large amount of didymium contained in it is coloured faintly pink, yields no emanation. But a thoroughly rested eye may also perceive the activity of this last precipitate on the luminous screen.§

The preparation of this material, which is to be obtained in great quantity, must be deferred to a future period. For the present research the mother-liquor freed from radium bromide, and the greater quantity of barium bromide, sufficed; this has already been render richer in the emanation substance, *i.e.*, it contains it least adulterated with inactive earths. The treatment of this consisted in dissolving in hydrochloric acid the precipitate obtained with ammonia, after removal of any barium precipitated with it by means of sulphuric acid, and evaporating to dryness on the water-bath. On taking up the residue after evaporation with water, several centigrammes of an insoluble residue remained behind, which yielded the most strongly active (emanation) substance yet obtained. This residue was not investigated but reserved for the physical experiments.

The filtrate gave with sulphuretted hydrogen only a small active precipitate which contained lead. The precipitate obtained afterwards with oxalic acid amounted to about 2 grms. after further purification, and was almost as inactive as the insoluble residue. The precipitate formed by adding ammonia to the filtrate, and the final precipitate consisting of magnesia formed on addition of ammonium carbonate, were less active. Also the small remaining residue left on driving off the fumes from the last filtrate after evaporation was very active.

All precipitates, with the exception of those formed by oxalic acid and sulphuretted hydrogen, showed emanation which generally increased in the first few days. The ammonia precipitate, as well as the magnesia precipitate, contained small impurities of rare earths, after separation of which the activity correspondingly diminished, and grew stronger in the latter.

The oxalate of these earths becomes almost white on ignition, with a very faint salmon tint, and is then easily soluble in hydrochloric acid. The solution is at first orange, and becomes colourless with evolution of chlorine; similarly the solution in nitric acid on addition of hydrogen peroxide, but only very little cerium is obtained as hydroxide by the hydrogen peroxide reaction. The concentrated solutions of the salts show no trace of an absorption spectrum, and thus are practically free from didymium. Potassium sulphate, as well as hydrogen peroxide, completely precipitates the solution of the potassium double salt, which last gives also an emanation. Thiosulphate gives no precipitate on boiling, only a very slight turbidity. Ammonium oxalate does not extract from the oxalate sufficient thorium to be precipitated by ammonia. After driving off the ammonium salt a trace remains, which, however, is not more active than the undissolved oxalate. But it is noteworthy that the oxalate thus treated then gives the emanation very strongly.

Like the lanthanum salt the chloride crystallises easily, is itself phosphorescent after removal of water, and shows the emanation. In the Bunsen flame only the sodium line is visible spectroscopically. The sulphate forms definite crystals, and has no emanation or phosphorescence. According to these reactions thorium cannot be present to any material extent, and the traces present cannot be the cause of the activity. Lanthanum appears to be the essential impurity. It may be mentioned that the percentage amount of this earth present in a new radio-active element must be about 0·1 per cent, if it be assumed that the Becquerel radiation possesses the same intensity and the same power of penetration as in the case of radium. The Becquerel radiation of the preparation thus affects the barium platinum cyanide screen in the same degree as a barium carbonate with about 0·1 per cent radium. For a smaller intensity and power of penetration of the linear radiation than in the case of radium the percentage content would of course be higher. Thus in the case in question about 2 grms. must contain at least 2 m.grms. of the element. From what has already been stated, this can be neither radium nor polonium. For the present I will not follow the custom, usually adopted from practical considerations, of giving a name to the hypothetical element, until it has been established how Debierne's substance (actinium), hitherto

* *Berichte*, 1902, xxxv., 3608.

† The only temporarily active rare earths previously separated by me (*Berichte*, 1900, xxxiii., 3570,; 1901, xxxiv., 3776) from uranium mineral, as well as from commercial uranium salts (*Berichte*, 1900, xxxiii., 1665) behaved in the same way as "ThX."

‡ In all researches I have only paid attention to the emanation when it can be observed on the zinc sulphide screen.

§ Commercial thorium preparations do not affect the luminous screen.

known only as thorium, also behaves as regards the emanation.

In the examination of the physical properties of the emanation substance the following results have been obtained:—

The linear Becquerel radiation is capable of being deflected, at any rate partly, by a magnet. No decrease in it could be observed in about six months, but rather—as far as my observations go to show—an increase, similar to that in the case of radium. The degree of power of emanation of different preparations in the same chemical compound is proportional to the intensity of their Becquerel radiation. Igniting for a short time does not destroy the power of emanation.

Glass vessels in which the substance is kept phosphoresce, and on opening them the smell of ozone is perceptible.

The strong and rapid inducing effect of the substance is very striking. Most objects, *e.g.*, paper, which are shut up in the same receptacle (as small as possible) with the substance, very soon exhibit the same characteristics as the substance itself. If the preparation wrapped in paper is held at the back of the platinum cyanide screen for half to one minute the spot in question becomes luminous for a short time. No luminosity appears on laying on the varnished side of the screen.* This induction was clearly produced, not by the Becquerel radiation of the preparation, but by the emanation; it can be regarded as an absorption of the emanation, and is thus more easily perceived in porous substances, such as paper. The moisture present in the substance plays an important part in it. Wet filter-paper is made more strongly and lastingly active than dry. Impregnation with aqueous ammonia or hydrochloric acid gives the same result as with water.

By means of a current of air the emanation can be extended, so that the usual screens if they are unvarnished or prepared with gelatin (which absorbs the fumes) are rendered luminous by it. The phosphorescing zinc sulphide is best adapted for this purpose. The current of air momentarily discharges an electroscope. A thin film of celluloid intercepts the emanation.

If the preparation is laid in a cylindrical metallic capsule, closed at one end, and this is held vertically with the opening downwards towards a zinc sulphide screen negatively charged by an influence machine at a distance of from 5 to 10 c.m. from it, a diminished phosphorescence image of the opening of the capsule appears on the screen. This is brighter at the edge than in the middle. By inclining the screen, an elliptical instead of a circular surface is projected. A square opening gives an image in the form of a square with each of the sides slightly depressed in the centre.

If the opening of the capsule is diminished to any desired form, *e.g.*, by means of shaped shutters, very sharp, still more clearly and homogeneously luminous diminished images of the openings are obtained. The phosphorescent image so affects the screen that it becomes luminous for a long lime, and gives secondary emanation. If the capsule is insulated, the image becomes fainter. A current of air, which only extends the secondary emanation, no longer influences the position of the image. Direct convergence of the "beam of rays" could not be established; only a grouping together apparently takes place; generally the image is smaller for greater distances between screen and capsule. If the image is approached by a conductor connected to earth, in consequence of the positive charge induced by the negative screen, repellence takes place. The image is deformed to a straight or semi-circular line, according to the shape of the conductor; the space between it and the conductor amounts to 1 to 2 c.m. A dielectric rod held between the screen and capsule does not repel so energetically, and only casts an enlarged shadow. If a wire net connected to earth (which interrupts the electric field) is held in the place of the rod, the screen remains dark; on insulating the wire net the emanation penetrates.

All the phenomena are the same if the screen is negatively charged and the capsule connected to earth, or if, conversely, the capsule is positively charged and the screen connected to earth.

From these experiments it follows that the emanation experiences in the electric field an acceleration in direction from the positive to the negative electrode. The emanation changes into a radiation; it must itself possess a positive charge.

Up to the present, with the means at my disposal, I have not been able to perceive any effect caused by a magnet in the emanation, which is influenced by the electric field.

The question whether the emanation is to be regarded as the positive ions, and the new radiation as a parallel to the channel radiation, or S_1 radiation of E. Goldstein (*Verh. d. Dtsch. Phys. Ges.*, 1902, iv., 228), or whether the emanation is simply the vapour of the substance itself, which, according to Curie's researches on radium, can itself assume a positive charge, may be left undecided. In any case, the emanation of my substance is very different from that of radium, which does not cause the phenomena described. I should suggest calling the new rays "E rays."

The measurement of the flame spectrum of radium Professor Runge has most kindly undertaken. He will report on it in *Drude's Annalen*, 1903, II., 1.

According to Professors Runge and Bodländer, the gas constantly evolved from solutions of radium bromide is essentially hydrogen.*

The following communication comes from Professor Bodländer:—

"The solution of 1 grm. of the 5 per cent radium preparation sent to me gave off 3·5 c.c. of gas in sixteen days. Seventy-eight per cent of this gas was hydrogen, and 17 per cent oxygen, while the solution became coloured brown by bromine. Thus a sort of electrolysis† occurs under the influence of the radium, in that the negative electrons change the hydrogen ions into neutral molecules, while by the positive electrons, bromine or hydroxyl ions are discharged. The experiments on the duration of the evolution of gas under different conditions will be continued, so that the source of the not inconsiderable energy (1·8 watt-seconds = 0·43 cal. = 18000 g.c.m. daily) obtained from about 5 c g. of radium bromide may be explained."—*Berichte der Deutsch. Chem. Ges.*, 1903, xxxvi., 342.

Some Complex Compounds of Uranic Acid.—H. Itzig.—According to M. Kohlschutter, the tartrate of uranium prepared by Peligot should have the formula $C_4H_4O_6UO_3+3H_2O$ and not $C_4H_4O_6UO_2+4H_2O$. From the rotatory power of his solutions, which is seven times as much as that of tartaric acid, and also because of the fact that the reactions of tartaric acid and uranium are masked therein, the author is inclined to look upon this product as a urano-tartaric acid, $CO_2H(CHOH)_2CO_2UO_2OH$, a monobasic acid, of which the potassic salt is contained in uranic acid solution in the monopotassic tartrate. In the same manner we have a uranomalic acid, $CO_2H.CH_2.CHOH.CH_2UO_2OH$, of which the sodium salt has been obtained as a yellow, amorphous mass, very soluble in water, containing $2H_2O$. The rotatory power of malic acid is increased thirty times by the addition of uranium.—*Berichte*, vol. xxxiv., p. 3822.

* Only a pure radium salt with the highest activity produces a brief luminosity of the platinum cyanide, but it is immaterial which side of the screen was exposed to the radium.

* Two Geisler tubes which I had previously filled with radium gas (one with gas from solution and the other with gas from crystals) showed the hydrogen lines as plainly as possible. I did not then mention this, because it was not certain that the gas was absolutely free from water.

† (Author's note). The behaviour of radium solutions discovered by me (*Ann. d. Phys. u. Chem.*, 1899, lxix., 92) with regard to the radiation, as opposed to that of the solid salt, may be thus explained. The energy of the radiation is manifested in the solution more in the form of a decomposition of the water, and less as Becquerel radiation.

THE DETERMINATION OF STRYCHNINE AND BRUCINE IN *NUX VOMICA*.

By EDWIN DOWZARD, F.C.S.

Part I.—The Determination of Strychnine.

The method which has been most used for the determination of strychnine in the presence of brucine is the ferrocyanide process of Dunstan and Short. This process depends on the fact that when potassium ferrocyanide is added to the solution of a salt of strychnine, the ferrocyanide is precipitated as a white crystalline powder, only very sparingly soluble in cold water. The ferrocyanide of brucine is much more soluble than the strychnine salt.

The great objection to this process is that the brucine is more or less completely precipitated after standing for some time. This method, which has been adopted by the British Pharmacopœial authorities, has been criticised by Farr and Wright ("Year-book of Pharmacy," 1900), who state that unless the precipitation of the strychnine ferrocyanide takes place at a constant temperature, and the wash-water is always of the same amount and temperature, that constant results cannot be obtained, and that only when certain conditions are observed is it possible to obtain accurate results. Farr and Wright have suggested that the mixed ferrocyanides should be washed with 200 c.c. of acidulated water at 38° C., and that a correction be applied for the amount of strychnine dissolved. The weight of the mixed alkaloids, temperature at which precipitation takes place, volume and temperature of wash-water, size of filter-paper, speed of filtration, and volume of each washing, must all be taken into consideration. There are so many details which must be observed before accurate results can be obtained, that this method cannot be recommended for general use.

After trying various methods, I found that the nitric acid method gives the best results. This process depends on the following facts:—When strychnine is dissolved in dilute sulphuric acid and the solution treated with nitric acid, the alkaloid remains practically unaffected, and may be extracted with chloroform after the liquid has been made alkaline. When brucine is treated in the same manner, it is decomposed, and nothing—or practically nothing—can be extracted with chloroform.

The following is a description of the procedure I have found to give the most accurate results. The details of this method were fixed on after a large number of experiments:—

The mixed alkaloids must be first obtained in a practically pure state.

For extracting the alkaloids from *Nux vomica* seeds, a slight modification of Dunstan and Short's method may be used, which is as follows:—Mix 5 to 10 grms. of powdered *Nux vomica* seeds with a solution of 2 grms. of sodium carbonate (anhydrous) in 10 c.c. of water. Dry over a water-bath and reduce to powder. Exhaust this in a Soxhlet apparatus with a mixture of 3 parts chloroform and 1 part absolute alcohol until a small quantity of the percolate, on evaporation, yields a bitterless residue. Transfer the clear solution (filtered if necessary) to a separating funnel (stoppered), add 15 c.c. 4 per cent H_2SO_4, shake for five minutes, separate, and repeat twice, using 10 c.c. each time; filter the acid solution (mixed) through a cotton-wool plug, add excess of ammonia to the filtrate, and extract three times with chloroform (using 15 c.c., 10 c.c., and 5 c.c). The chloroformic solution is then passed through a small filter, the filter being washed several times with chloroform; the alkaloids are obtained on evaporation. The last traces of solvent should be removed by blowing air into the flask. The mixed alkaloids should be heated as little as possible.

The alkaloids are obtained from the liquid extract as follows:—Measure 5 c.c. of the sample into a small porcelain basin, add 10 c.c. of water, and evaporate to about 5 c.c. on a water-bath; add 5 c.c. of water and one drop of 20 per cent H_2SO_4, heat on bath for about two minutes, stirring continuously; then transfer to a separator, rinse out basin several times with small quantities of hot water, pour 5 c.c. of chloroform into the basin, and rub any adhering resinous or fatty matter with a glass rod until dissolved; transfer to separator, and repeat twice with 5 c.c. of chloroform; finally rinse the basin out with a few c.c. of hot water. The liquid should be kept as low in bulk as possible. Add to contents of separator 2 grms. of sodium carbonate (anhydrous) dissolved in 5 c.c. of water, shake for five minutes, heat separator by placing in a large beaker of water at 65° to 70° C.; the stopper should be occasionally removed to relieve the pressure (if these instructions are followed, a sharp clear separation will in most cases be obtained in a few minutes); separate the solvent, and extract the alkaline solution twice with chloroform, using 10 c.c. each time; heat to aid separation. Shake the mixed chloroform washings for one minute with 2 grms. of sodium carbonate dissolved in 15 c.c. of water; heat mixture to aid separation. This washing is to free the solvent from colouring matter. Extract the chloroform three times with 4 per cent H_2SO_4, using 10 c.c. each time; filter acid solution through a cotton-wool plug, washing the plug several times with water. The filtrate is made alkaline with ammonia and extracted three times with chloroform, using 10 c.c. each time. The solvent is filtered through a cotton-wool plug (fat free), and the plug washed several times with chloroform. The filtering apparatus I use for this purpose is made as follows:—A small hole is blown in the bottom of a test-tube, cotton-wool (fat free) is then packed into the tube until a column of about 2 to 2·5 c.m. is obtained. The liquid to be filtered is poured into the tube, the filtrate being conducted to the separator by a small funnel. The speed of filtration may be increased by placing the lips over the mouth of tube and blowing. The chloroformic solution is now shaken for twenty seconds with 15 c.c of water containing one drop of ammonia (sp. gr. 0·890); the alkaloids are obtained as described before.

The mixed alkaloids having been obtained in a pure state, the separation of the strychnine is effected as follows:—Dissolve the mixed alkaloids in 25 c.c. of 2 per cent H_2SO_4 (heat, if necessary, to aid solution), filter, and wash the filter-paper with 2 per cent H_2SO_4 until the filtrate measures 50 c.c.; cool to ordinary temperature (15—25° C.), and add 5 c.c. of nitric acid (sp. gr. 1·42); mix well, allow to stand for fifteen minutes, pour into a separator containing 15 c.c. ammonia (sp. gr. 0·890) and 10 c.c. of chloroform, shake mixture for five minutes; after separation has taken place, the solvent is transferred to another separator and the alkaline liquid again extracted with 10 c.c. of chloroform.

To 44 c.c. of water add 1 c.c. of ammonia (sp. gr. 0·890). The chloroformic solution is shaken for twenty seconds with 15 c.c. of the above dilute ammonia solution. After separation has taken place, the solvent is transferred to another separator; this treatment is repeated twice. (The chloroformic solution is washed with dilute ammonia to free it from a small quantity of colouring matter). The solution of strychnine is transferred to a tared wide-mouthed short-necked flask (capacity about 150 c.c.), the solvent is distilled off until about 1 c.c. is left, 1 c.c. of

Weight of alkaloids taken.		Strychnine found.
Brucine.	Strychnine.	
0·0500	0·0500	0·0500
0·0500	0·0500	0·0501
0·0500	0·0750	0·0749
0·0500	0·0750	0·0750
0·0750	0·0750	0·0751
0·0750	0·0750	0·0750
0 0750	0·1500	0·1499
0·1500	0 0750	0·0753
0·1500	0·1500	0·1501
0·1500	0·1500	0·1502

absolute alcohol is added, and the flask placed in an air-bath kept at a temperature of about 80° C.; when the last trace of alcohol has been driven off, the temperature is raised to 100° C. The flask is weighed till constant.

The accuracy of this method was proved by the experiments shown in Table.

Part II.—The Determination of Brucine.

The most distinctive reaction of brucine is the production of a red colour with nitric acid. This, I thought, might be useful as a means of determining brucine in the presence of strychnine, as the latter alkaloid is not affected by nitric acid, only a slight yellow colour being produced on standing. The following method was decided on after a large number of experiments.

A solution is made containing 0·16 grm. brucine (anhydrous) and 0·16 grm. strychnine in 100 c.c. of 2 per cent H_2SO_4. The mixed alkaloids are obtained as described in Part I. of this paper. The filtered chloroformic solution of the pure alkaloids is not distilled, but made up to 50 c.c. Ten c.c. of this solution is evaporated to dryness in a tared beaker, and the residue dried at 105—110° C, till constant in weight. The remaining 40 c.c. is distilled until about 1 c.c. is left in the flask; this is removed by blowing air into the flask and heating gently. If the alkaloids are heated too strongly they turn a light brownish colour, which interferes with the results. The weight of mixed alkaloids is calculated from the weight obtained from 10 c.c. The colourless alkaloidal residue is dissolved in 25 c.c. of 2 per cent H_2SO_4, heating gently to aid solution. The liquid is filtered into a graduated cylinder, and the filter-paper washed with 2 per cent H_2SO_4 until the filtrate contains 0·1 grm. mixed alkaloids in 50 c.c.

Fifty c.c. of the standard brucine solution and 50 c.c. of the liquid containing 0·1 grm. mixed alkaloids are placed in two small beakers, 5 c.c. of nitric acid (sp. gr. 1·42) is added simultaneously to the contents of each beaker, the mixtures are agitated, and transferred to the comparison troughs of a Gallenkamp colorimeter. Five minutes after the addition of nitric acid the liquids are compared, the mean of six readings is taken, and the amount of brucine calculated. Fifty c.c. of the standard brucine solution contains 0·08 grm. brucine; this equals 100 on the colorimeter scale. If the solution of mixed alkaloids gave a reading of 60 on the scale, the amount of brucine present in 0·10 grm. mixed alkaloids would be 0·048 grm. (100 : 60 :: 0·08 : 0·048). Before this instrument (Gallenkamp's colorimeter) is used, it should be standardised by a brucine solution of known strength. If possible the observations should be made by daylight; good results, however, can be obtained by gas-light. The light should be reflected from a piece of white cardboard. Care must be taken that the light is perfectly diffused; otherwise, accurate results cannot be obtained. The accuracy of this method was proved by the following experiments :—

Alkaloids taken.		Colorimeter readings.	Brucine found.
Strychnine.	Brucine.		
0·0500	0·0500	(63·5, 63·0, 63·5, 62·5, 63·0, 63·0) .. .. 63·08	0·0504
0·0600	0·0400	(50·5, 49·5, 50·0, 50·5, 50·5, 50·5) .. .. 50·25	0·0402
0·0700	0·0300	(37·5, 37·5, 37·5, 37·0, 38·0, 37·5) .. .. 37·50	0·0300
0·0300	0·0700	(88·5, 88·0, 87·5, 88·0, 87·5, 88·0) .. .. 87·91	0·0703
0·0400	0·0600	(76·0, 76·0, 76·5, 75·0, 75·5, 76·0) .. .. 75·83	0·0606

The determination of the strychnine and brucine by the methods given above may be made on the same portion, thus placing a check on the results. In this case, 10 grms. of the powder, or 10 c.c. of the liquid extract, should be operated on, as described in Part I.

The filtered chloroformic solution of mixed alkaloids is made up to 50 c.c.. Ten c.c. is evaporated, and the residue dried at 105—110° C. for total alkaloids. The remaining 40 c.c. is evaporated to dryness as described before, dissolved in 40 c.c. of 2 per cent H_2SO_4, filtered, and the filter-paper washed with 2 per cent H_2SO_4 until the filtrate measures 100 c.c. Fifty c.c. of this solution is used for the determination of strychnine, the amount of mixed alkaloids in the remaining 50 c.c. is calculated, and the solution diluted until 50 c.c. contains 0·1 grm.; the brucine is then determined as above.

In the following example I have given the figures obtained in the examination of a sample of *Nux vomica* powder. The strychnine, brucine, and total alkaloids were determined separately.

Nux vomica Powder.

50 c.c. chloroform = alkaloids from 10 grms. of sample.
10 c.c. of above = 0·064 grm. mixed alkaloids = 3·2 per cent.

The remaining 40 c.c. was evaporated, and the residue dissolved in 100 c.c. 2 per cent H_2SO_4.

50 c.c. of above = 0·0585 grm. strychnine = 1·462 per cent.
50 c.c. of above = 0·1280 grm. mixed alkaloids; after diluting to 64 c.c., 50 c.c. = 0·100 mixed alkaloids.
Average of six readings, 67·5 (100:67·5 :: 0·08:0·054);

$$\frac{0{\cdot}054 \times 3{\cdot}2}{0{\cdot}1} = 1{\cdot}728 \text{ per cent brucine.}$$

	Per cent.
Found—Total alkaloids	3·200
Strychnine	1·462
Brucine	1·728
Brucine calculated	1·738

The greater part of the expense of this investigation was defrayed by means of a Government grant.

THE SPECIFIC HEATS OF METALS AND THE RELATION OF SPECIFIC HEAT TO ATOMIC WEIGHT.*

Part II.

By W. A. TILDEN, D.Sc., F.R.S.,
Professor of Chemistry in the Royal College of Science, London.

The following values have been obtained for the mean specific heats of pure aluminium, nickel, cobalt, silver, and platinum, within the several limits of temperature indicated :—

Centigrade.	Aluminium.	Nickel.	Cobalt.	Silver.	Platinum
−182° to +15°	0·1677	0·0838	0·0822	0·0519	0·0292
−78 ,, +15	0·1984	0·0975	0·0939	0·0550	—
+15 ,, 100	—	0·1084	0·1030	0·0558	0·0315
15 ,, 185	0·2189	0·1101	0·1047	0·0561	—
15 ,, 335	0·2247	—	—	—	—
15 ,, 350	—	0·1186	0·1087	0·0576	—
15 ,, 415	—	0·1227	—	—	—
15 ,, 435	0·2356	0·1240	0·1147	0·0581	0·0338
15 ,, 550	—	0·1240	0·1209	—	—
15 ,, 630	—	0·1246	0·1234	—	—
0 ,, 1000	—	—	—	—	0·0377*
0 ,, 1177	—	—	—	—	0·0388*

* Violle (*Comptes Rendus*, 1877, vol. lxxxv., p. 543; also *Phil. Mag.* [5], vol. iv., p. 318).

From these results the specific heats at successive temperatures on the absolute scale have been calculated, and

* Abstract of a Paper read before the Royal Society, Dec. 11, 1902.

it appears that the assumption of a constant atomic heat at absolute zero is untenable.

The mean specific heat of a sample of nickel steel, containing 36 per cent of nickel and having remarkably small dilatation, was found to be as follows:—

Range of temperature.	Mean specific heat.
−182° to +15°	0·0947
15 ,, 100	0·1204
15 ,, 360	0·1245
15 ,, 600	0·1258

The mean specific heats of the sulphides of nickel and silver were also determined with the object of getting some evidence as to the cause of the difference observed between the two metals in regard to the influence of temperature on their respective specific heats. The following are the values obtained:—

Range of temperature.	NiS.	Ag_2S.
−182° to +15°	0·0972	0·0568
15 ,, 100	0·1248	0·0737
15 ,, 324	0·1333	0·0903

The mean value for the specific heat of silver sulphide is less than that for nickel sulphide throughout, but little can be deduced from the results till the influence of temperature on the specific heat of sulphur is known.

THE EVAPORATION OF WATER IN A CURRENT OF AIR.*

By EDGAR PHILIP PERMAN, D.Sc., F.C.S., Assistant Lecturer in the University College of South Wales and Monmouthshire.

The object of this investigation was to discover with what accuracy the vapour-pressure of water could be calculated from the amount of water vapour carried off by an air current passed through the water, the temperature being maintained constant. The method adopted was to aspirate air, at a rate of not more than 0·1*l.* per minute, through a succession of wash-bottles containing water and placed in a thermostat. The water carried off by the air was absorbed by means of concentrated sulphuric acid, and weighed. The vapour-pressure was calculated from the expression:—

$$V.p = \frac{W \times 1{\cdot}242 \times 760 \times P \times T}{T(W \times 1\,242 \times 760) + 273 \times V \times p};$$

where W = Weight of water drawn off.
P = Pressure in the last wash-bottle.
T = Absolute temperature of air in aspirator.
V = Volume of air drawn through the water, measured at temperature and pressure of aspirator.
p = Pressure of air in aspirator.

The results obtained show in every case a close agreement between the calculated vapour-pressure and that commonly accepted. Experiments were made at temperatures varying from 20° to 90° C. It may be concluded from this that in air saturated with moisture (under the conditions used in the experiments) the pressure of the aqueous vapour is the same as the vapour-pressure of water when no other gas is present, also that the density of the aqueous vapour in the mixture is normal. It follows also that the density of saturated aqueous vapour, *without* admixture of any other gas, is approximately normal. This conclusion is confirmed by calculations of the density from the thermo-dynamical equation—

$$L = \frac{T}{J}(s' - s)\frac{dp}{dT}$$

using Griffiths's values of L and J, and the latest determinations of vapour-pressure at the Reichsanstalt for the values of dp/dT.

A *resumé* is given of the various determinations of the density of saturated aqueous vapour.

* Abstract of a Paper read before the Roya Society, February 19th, 1903.

ANALYTICAL NOTES.

By EDMUND J. MILLS, D.Sc., F.R.S.

1. In the usual routine of qualitative separation, the filtrate, after passing hydric sulphide, is boiled and treated with nitric acid. If any iron be present, oxidation is imperfect, and some of the ferrous iron passes through the next group, to be precipitated by ammonic sulphide as "traces of nickel." For many years I have been in the habit of using bromine-water, which is a perfect oxidiser, instead of nitric acid. It also has this advantage—that the desired excess of it can be readily detected by sight and smell.

2. The precipitate with ammonic sulphide is generally very difficult to filter, owing to the presence of some sulphur compound, presumably the pasty hydric persulphide. The remedy usually prescribed is prolonged boiling. I have always found the addition of a few grms. of sodic sulphite to the hot liquid (with precipitate) produce immediate clarification. As the metallic sulphides do not dissolve, this plan may be adopted for quantitative work.

A REACTION OF CACODYLIC ACID AND THE CACODYLATES.

By J. BOUGAULT.

Very few positive reactions are known with cacodylic acid and the cacodylates; the ordinary reagents do not precipitate them, with the exception of mercurous nitrate, which gives a precipitate with the cacodylates, at first white and almost immediately becoming yellow. I should mention also Barthe and Péry's reaction described in the "Manipulations de Pharmacie," by E. Gerard, p. 222.

The new reaction I am about to describe is very characteristic, very sensitive, and very easy to carry out. It enables us to detect traces of cacodylates, even when mixed with the methylarsenates, which resemble them very closely in their composition.

The reagent employed is the hydrochloric solution of hypophosphorous acid, that I have described already (*Journ. de Pharm. et de Chim.*, 1902, Series 6, vol. xv., p. 528) as being very sensitive in the detection of arsenic in the form of arsenites and arsenates, in the most varied products.

If we place a small quantity of cacodylate of sodium dissolved in about 1 c.c. of water in a test-tube, and then add about 10 c.c. of the reagent and cork up the tube, after a time, which varies with the proportion of cacodylate present, a very distinct cacodylic odour is developed. Even with half a milligrm. of cacodylate, this odour becomes perfectly distinct after a contact of twelve hours, and no deposit of arsenic is formed in the liquid. But with larger quantities of cacodylate, we observe, on the upper part of the test-tube above the surface of the solution, a deposit of arsenic which is produced slowly, and continues to increase for several days. I only mention this latter fact without laying any stress on it, as the odour is both more sensitive and more to be depended upon.

The methylarsenates behave in quite a different manner. They do not cause any cacodylic odour, and all the arsenic present is liberated and precipitated.

The presence of the methylarsenate does not interfere with the reactions of the cacodylate. But the inverse is

not quite the case, the reduction of the methylarsenate is less sensitive in the presence of a cacodylate than when the salt is pure.

In any case, these facts show that the hypophosphorous acid reagent can be utilised as follows:—

1. To detect cacodylic acid and the cacodylates, and especially for their detection in the presence of disodic methylarsenate:—We place 0·20 grm. of methylarsenate in a test-tube, and dissolve it in 2 c.c. of water, add 10 c.c. of the reagent, and leave in contact in the cold for twelve hours in the corked tube. At the end of this time a strong cacodylic odour is perceived, if the substance contains a cacodylate, even if the amount is only half a milligrm.

2. To detect the presence of other arsenical compounds in cacodylates:—We place 0·20 grm. of cacodylate of sodium in a test-tube, and dissolve it in 1 to 2 c.c. of water and 10 c.c. of the reagent. The pure cacodylate does not cause any colouration, or any deposit of arsenic in the liquid; the least trace of arsenic (less than a tenth of a milligrm. of arsenious acid or of arsenic) produces a brown colouration or a precipitate; it is advisable to keep to the dilution mentioned, viz., 1 to 2 c.c. of the aqueous solution to 10 c.c. of the reagent.—*Journ. de Pharm. et de Chim.*, Series 7, vol. xvii., No. 3.

ON THE

CAUSE OF THE DETERIORATION OF PLATINUM CRUCIBLES FROM THE CALCINATION OF AMMONIO-MAGNESIC PHOSPHATE.

By W. C. HERÆUS.

CHEMISTS who have frequently to calcine precipitates of ammonio-magnesic phosphate, often observe the deterioration of the platinum crucibles used for this operation.

The crucible cracks or flakes, the metal shows a crystalline structure in the fracture, and sometimes there are evidences of fusion; very often these faults are attributed to the quality of the metal, and apparently *à priori* with reason, inasmuch as the same deterioration is not observed in other laboratories.

M. Heræus, a manufacturer of platinum apparatus, who frequently has such complaints from his clients, has examined this question carefully, and, as a result of this examination, has arrived at the following conclusions:—

1. The quality of the platinum has no influence on its resistance; pure platinum and that alloyed with 10 per cent of iridium or rhodium does not last any better than the ordinary metal.

2. The phenomena observed are due to the formation of phosphorus.

3. Magnesic pyrophosphate is reduced by carbon at and above 950°, with the production of phosphorus.

4. The reducing gases, especially hydrogen, produce the same phenomena at 900°.

5. Ammonia which is dissociated at a high temperature is, on account of the hydrogen it contains, an eminently reducing gas.

6. The action of ammonia is the more intense if the precipitate contains an excess of ammonic phosphate; that is to say, if, owing to the conditions of precipitation, it contains the phosphate, $(NH_4)Mg(PO_4)_2$, described by Neubauer (*Zeit. f. Anorg. Ch.*, 1892, [2], p. 45, and 1893, [4], p. 251; *Zeit. f. Angew. Ch.*, 1896, ix., No. 14.

Thus the deterioration of platinum crucibles depends on the method of working followed in the estimation. The author leaves it to the chemists interested to decide which method to follow. It is evident, first of all, that it is necessary to proceed in such a manner as to prevent the formation of the precipitate of the mono-magnesic phosphate mentioned above; next in importance, it is necessary to prevent the ammonia given off during calcination coming in contact with the magnesic pyrophosphate at a high temperature. Thus, care must be taken to heat the precipitate of ammonio-magnesic phosphate very gently at first, and with the crucible uncovered, so as to get rid of the ammonia before the residue reaches the temperature at which reduction might take place.

It is not advisable to collect and calcine successively several precipitates of phosphate in the same crucible, as is the custom, especially when using a Gooch crucible; as a matter of fact, in such a case it may happen that the ammonia of the last precipitate may act on the pyrophosphate of the preceding estimation.

The method of procedure, which consists in treating the precipitate with nitric acid at once, so as to obtain the white pyrophosphate at the first onset, is evidently the best way to prevent any reduction, and consequently any attack of the platinum.—*Zeit. f. Angewandte Ch.*, 1902, xv., p. 917.

A COLOURED REACTION OF THE SALTS OF URANIUM AND PEROXIDE OF HYDROGEN.

By J. ALOY.

THE coloured reactions of the salts of uranium are not very numerous. The precipitation of the uranic salts by potash, and the subsequent solution of the precipitate by the alkaline carbonates, give only a slightly characteristic yellow liquid.

As for the action of ferrocyanide of potassium, it gives a precipitate of variable colour, according to the conditions of the experiment. Like the preceding one, this reaction is only applicable to solutions of the salts at maximum strength, and it is entirely hidden by the presence of numerous metals, and especially by traces of iron.

The method I am about to describe enables us, on the contrary, to recognise the presence of uranium very rapidly.

On adding peroxide of hydrogen and then carbonate of potassium, either in the solid state or in very concentrated solution to a compound of this metal, we obtain a solution which has a very beautiful red colouration.

This method is very general, and can be applied to not only the yellow salts, but also to the uranous compounds and even to the anhydrous oxides. Still, in this latter case, it is preferable first to transform the oxide into nitrate by means of nitric acid. Further, this reaction succeeds in the presence of metals whose salts give with carbonate of potassium a precipitate insoluble in an excess of the carbonate, which is the general rule.

Bicarbonate of potassium is not capable of replacing the neutral carbonate, and, under the same conditions, gives a yellow liquid which becomes red on heating.

The sensitiveness of the method can be increased by making use of the property of the red compound, of being insoluble in alcohol. If to the red solution obtained as I have shown, we add two or three times its volume of strong alcohol, we obtain a red precipitate, which collects rapidly at the bottom of the vessel used.

The same reaction may be used for the detection of peroxide of hydrogen. A soluble uranic salt, such as the nitrate, is treated with carbonate of potassium in sufficient quantity to dissolve the precipitate which is first formed. The addition of peroxide of hydrogen to this solution produces a beautiful red colouration. If we wish to detect traces of peroxide of hydrogen, it is better to operate in a different manner, and to make a solution of uranic nitrate in alcohol at 95°, and then add a few drops of the solution to be tested and a few crystals of carbonate. In the presence of peroxide of hydrogen either a red precipitate or a red liquid is formed, which collects at the bottom of the vessel.

The reaction I have described takes place in two phases. In the first phase, the peroxide of hydrogen transforms the uranium compound into the white peruranic hydrate; in the second, this hydrate is decomposed by the alkaline carbonate. We know, from the work of Fairley, and the more recent researches of Mélikoff and Pissarjewsky, that the simultaneous action of peroxide of hydrogen and the alkalis on the uranic salts, gives rise to the formation of yellow per-uranates insoluble in alcohol. By using very dilute solutions of soda in the presence of alcohol, Fairley obtained a red oily liquid which he looked upon as a mixed per-uranate of uranium and sodium. I have repeated Fairley's experiment, operating as much as possible out of contact with water; for this purpose I treated a solution of the nitrate in ether with strong peroxide of hydrogen, and then with an alcoholic solution of soda. Under these conditions I obtained a red precipitate similar to that produced by the action of carbonate of potassium.

These red bodies consist of heavy precipitates which adhere very strongly to the sides of the vessel in which they are formed. They are very unstable, and lose a portion of their oxygen very rapidly at the ordinary temperature. They are soluble in water and insoluble in alcohol and ether. I have attempted to make use of their insolubility in alcohol to separate them in a definite form, but without success, for the solution in water and the precipitation by alcohol are accompanied with a partial decomposition of the compounds, which lose oxygen as well as their original red colour. Nevertheless, by substituting treatment with methylic alcohol for the treatment with water and ordinary alcohol, I succeeded in preparing red peroxidised compounds of uranium having a crystalline appearance, which I am examining at the present time.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 14.

THE FIFTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY, BERLIN, 1903.

It will be remembered that the first of these International Congresses was held at Brussels in 1894, this was followed by three others at Paris in 1896, Vienna in 1898, and Paris again in 1900. Berlin has been selected as the meeting-place for the fifth Congress, and this will be held from June 2nd to 8th, 1903, under the Presidency of Dr. Otto N. Witt.

The meetings of the Congress will take place in the Imperial Parliament House, the general meetings being held in the large hall. Like its predecessors, the Congress will be divided into sections, the meetings of which will be held in the Committee rooms of the House.

The Congress begins with an inaugurative evening reception on Tuesday, June 2nd; on Wednesday, June 3rd, the first General Meeting will be held at 10 a.m.; in the afternoon the Sections begin their work, and this will be continued on June 4th. On Friday, June 5th, a second General Meeting will be held at 10 a.m., when an Address will be delivered by Professor Henri Moissan, President of the Fourth Congress. On Friday afternoon and Saturday the meetings of the sections will be continued; on Sunday, the 7th, there will be a general excursion. The meetings of the sections will be continued and finished on Monday morning. In the afternoon the third General Meeting will be held, in which the business of the Congress will be discussed and brought to a conclusion. Besides the above meetings there will be a number of social arrangements, of which full particulars will be given.

The object of these International Congresses is to promote both the scientific and economic interests of chemical work by introducing uniform standard methods and regulations throughout the world. They propose to elucidate the points of view which are of importance for Government regulations concerning transport and duties. They are also intended to provide an opportunity for the mutual understanding of different branches of chemical work, as well as to improve the personal acquaintance between the representatives of the various branches of chemical work in different countries.

The English Section will be represented on the Organising Committee by the following gentlemen:—The Royal Society by Professor J. Emerson-Reynolds, Professor H. E. Armstrong, W. H. Perkin, and T. E. Thorpe. The British Association for the Advancement of Science by Professor James Dewar, Sir Henry Roscoe, and Professor R. Meldola. The Royal Society of Edinburgh by Professor John Gibson, J. B. Readman, and James F. Pullar. The Royal Institution by Sir William Crookes, George Matthey, and Dr. Ludwig Mond. The Chemical Society by Professor William Tilden, Professor W. R. Dunstan, Alexander Scott, and W. H. Perkin, jun. The Society of Chemical Industry by Ivan Levinstein, Thos. Tyrer, and Walter F. Reid. The Institute of Chemistry of Great Britain and Ireland by Professor J. Millar Thomson, G. T. Beilby, and Julius Lewkowitsch. The Iron and Steel Institute by R. A. Hadfield, J. E. Stead, and Bennett H. Brough. The Royal Agricultural Society by Aug. J. Voelcker. The Society of Public Analysts by Otto Hehner and Bertram Blount. The Federated Institute of Brewing by A. Gordon Salamon and Cornelius O'Sullivan; and the Honorary Secretary of this Joint Committee will be Mr. F. E. Armstrong.

The Congress will be divided into eleven Sections as follows:—Section I., Analytical Chemistry, Apparatus and Instruments. Section II., The Chemical Industry of Inorganic Products. Section III., Metallurgy, Mining, and Explosives. Section IV., The Chemical Industry of Organic Products, divided into Sub-sections, A, On Organic Products, including Coal-tar Products, and, B, Dye-stuffs and their Applications. Section V., The Sugar Industry. Section VI., Fermentation and Starch Manufacture. Section VII., Agricultural Chemistry. Section VIII., Hygiene, Medicinal and Pharmaceutical Chemistry, the Chemistry of Alimentary Products. Section IX., Photographic Chemistry. Section X., Electro- and Physical Chemistry. Section XI. Legal and Economic Problems referring to Chemical Industry. The subscription is 20 marks (£1) for the whole Congress, and for ladies, who may take part in the social arrangements, 15 marks (15s). Full particulars may be obtained on application to the Office, 21, Marchstrasse, Charlottenburg, bei Berlin.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending January 31st, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Charles Perrin, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, February 10th, 1903.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 220 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from January 1st to January 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Com-

bustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 220 samples examined by us during the month, all were found to be clear, bright, and well filtered.

For the first time since June, 1900, we have to record an excess of rain at Oxford, the actual rainfall during January has been 2·58 inches; the average fall is 2·08 inches; this gives an excess of 0·5 inch, or 19·3 per cent for the month, on the thirty-five years' average.

Our bacteriological examinations of 377 samples have given the results recorded in the following table; besides these we have examined 197 other samples, from special wells, standpipes, &c., making a total of 574 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	319
New River, filtered (mean of 78 samples) ..	13
Thames, unfiltered (mean of 26 samples) ..	13161
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 193 samples)..	69
Ditto ditto .. .. highest	562
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 27 samples) ..	313
River Lea, from the East London Company's clear-water wells (mean of 27 samples) ..	38

Of the 298 daily samples taken from the filter-wells of the Metropolitan Water Companies, and examined bacteriologically by us, thirteen samples, or 4·3 per cent, were sterile; forty-five samples, or 15·1 per cent, contained more than 100 microbes per c.c.; and twenty-one of these samples contained more than 150 microbes per c.c. The mean number of microbes in the forty-five samples containing more than 100 microbes was 198, against a corresponding mean of 177 in twenty-three samples in December.

Owing to the great increase in the rainfall during the last month, the microbes in the unfiltered Thames water have risen from about 6000 to 13,000, that is, the bacteriological impurity has about doubled, whereas the unfiltered New River water has undergone little or no alteration. The result of this increase has been that the filters of the Thames-derived Companies, which were not working at their best, furnished a larger number of samples from the filter wells, showing an increase in the number of microbes. In our last Report we pointed out that this would be the inevitable result in the event of an increased rainfall.

In comparison with last month there has been a small increase in the soluble organic matter, and the average colour due to this cause has been correspondingly increased.

It is of interest to compare the quality of the supply during last month, which was abnormally wet, with that of January, 1902—one of the driest months of that exceptional year. In January, 1902, the organic matter was about two-thirds of the present amount, while the bacteria amounted to about one-half. In neither case, in the majority of the samples, did the microbic impurity exceed what is allowable in a good and wholesome water.

We are, Sir,
Your obedient Servants,

William Crookes.
James Dewar.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Annual General Meeting, February 13th, 1903.

Prof. S. P. Thompson, President, in the Chair.

The following Report of the Council for the year 1902 was read:—

Since the last Annual General Meeting of the Society the usual number of meetings has been held. One of these, on June 13th, 1902, was held at the National Physical Laboratory at Bushy House, on the kind invitation of the Director, and was well attended in spite of a downpour of rain; another, on November 28th, was held at the Royal College of Science, by the invitation of Professor Callendar; and that which should have been held on June 27th took place on June 20th, owing to the fact that the former day had been declared a National Holiday.

The Society has to mourn the loss of several Fellows by death. Among these occur the names of Sir F. Abel, Dr. J. H. Gladstone, the first President of the Society, Mr. G. Griffith, long an active member of the Council, Sir W. Chandler Roberts-Austen, first Secretary of the Society, and Mr. James Wimshurst. Memoirs of some of these will be found in the Proceedings. Professor Cornu and Professor R. Felici, Hon. Fellows of the Society, also died during the year.

The Council also regrets that, owing to the calls of business, Mr. Elder has found it necessary to resign the post of Secretary. They feel that the Society owes a debt of gratitude to Mr. Elder for the energy and devotion with which he has ministered to the interest of the Society during the last decade.

There have been four resignations, and eleven new Fellows have been elected. The numbers are therefore well maintained.

The Bulletins of the Proceedings of the Meetings have been sent out regularly in accordance with the terms of Mr. Stanley's generous gift to the Society.

A new agreement for a term of three years has been arranged between the Society and the Institution of Electrical Engineers to provide for the continuation of *Science Abstracts*, and it is hoped that the usefulness of this publication will be thereby increased.

The Treasurer presented the balance-sheet together with the following report:—

The receipts for the present year do not include any exceptional sources of revenue such as life-compositions or donations. On the other hand, there are additional sources of expenditure, (1) on the International Catalogue £16 4s. 9d, (2) on the printing and distribution of abstracts of proceedings, about £35. In spite of this the bill for printing has been somewhat below the average, so that the revenue has just balanced the expenditure. The difference between the bank balance of £167 13s. 3d. at the beginning of the year and the balance of £68 6s. 6d. at the end of the year, is satisfactorily accounted for by the investment of about £98 from the current account, in addition to £571 10s. 5d. from the deposit account, in the purchase of Great Eastern Railway Debentures. By this purchase and the gift of L. B. & S. C. Ry. stock from Mr. W. F. Stanley, the revenue of the Society from investments has been materially increased, and will next year amount to about £115. The payments made to *Science Abstracts* next year will be reduced to about £256 under the new agreement with the Institution of Electrical Engineers. Thus, although some increase in the printing bill may be expected, it is probable that the revenue will continue to balance the expenditure.

The following Officers and Council were elected for the ensuing year:—

President—R. T. Glazebrook, D.Sc., F.R.S.

Vice-Presidents—Those who have filled the Office of President together with T. H. Blakesley, M.A.; Prof. J. D. Everett, D.C.L., F.R.S.; S. Lupton, M.A.; J. Swinburne.

Secretaries—W. R. Cooper, M.A.; W. Watson, D.Sc., F.R.S.

Foreign Secretary—Prof. S. P. Thompson, D.Sc., F.R.S.

Treasurer—Prof. H. L. Callendar, M.A., F.R.S.

Librarian—W. Watson, D.Sc., F.R.S.

Other Members of the Council—C. Chree, D.Sc., F.R.S.; W. B. Croft, M.A.; F. G. Donnan, M.A., Ph.D.; H. M. Elder, M.A.; R. A. Lehfeldt, D.Sc.; Prof. J. Perry, D.Sc. F.R.S.; A. W. Porter, B.Sc; W. A. Price, M.A.; W. F. Stanley, F.G.S.; W. C. D. Whetham, M.A., F.R.S.

Dr. R. T. Glazebrook then took the Chair and delivered an Address. After thanking the Members for electing him to the office of President he referred to the work of Gladstone, Roberts-Austen, Griffith, and Wimshurst, four Fellows whom the Society had lost by death since the last General Meeting. The Society had also lost two Honorary Fellows in Ricardo Felici and Alfred Cornu. Stokes was not a Fellow of the Physical Society. The Society regretted it, and were poorer for it, Turning to domestic affairs, Dr. Glazebrook mentioned the retirement of Mr. Elder, after ten years' work as Secretary. The membership of the Society was almost stationary instead of increasing, and it was necessary to consider how best to further the interests of the Society. It should have a wider range of activity, and technical papers should not necessarily be excluded. If possible all papers should be sent out, in full or in abstract, before any meeting, so as to encourage discussion. Interest might also be aroused by arranging at times for set discussions. The Society was at a disadvantage in having no home of its own, and the time of meeting might be reconsidered. Attempts should be made to give advice and guidance to physicists in isolated positions about the country having time to carry out research. The rest of the Address dealt with the history of theoretical optics during the last sixty years, and the part taken by Stokes in its development.

The Society then adjourned until February 27th.

NOTICES OF BOOKS.

An Introduction to the Study of Metallurgy. By Sir W. C. Roberts-Austen, K.C.B., F.R.S., &c. Fifth Edition, Revised and Enlarged. London: Charles Griffin and Co., Ltd. 1902. Pp. 516.

This volume is one of a seriee of treatises written by Associates of the Royal School of Mines, and the fact that it is now in its fifth edition affords ample evidence of the appreciation it has met with at the hands of students, practical metallurgists, and chemists.

Sir William Roberts-Austen, whose lamented death at the latter end of November last is still fresh in our memories, was perhaps the foremost metallurgist of his day, and had made his mark not only as a scientific worker but as a teacher of metallurgy.

There is no need to recapitulate here the contents and arrangement of this volume; it is already known and appreciated by all metallurgists, and we can do no more than heartily recommend its careful perusal to students, coupled with the regret that they will be unable to share with their predecessors the advantages of the personal assistance and teachings of the late professor of metallurgy at the Royal School of Mines.

We must point out an evident oversight in the date of the preface to this edition; it is given as "December, 1902," and as Sir W. Roberts-Austen's death occurred on November 22nd last, it would give the impression that he was not the writer of the preface, though from its wording t was evidently his work,

A Text-book of Quantitative Chemical Analysis. By Frank Julian. First Edition. Illustrated. St. Paul, Minn.: The Ramsey Publishing Company. 1902. Pp. 604.

This volume is divided into four principal parts and an appendix, and is intended for the use of students who, having a fair acquaintance with the elements of general chemistry, can devote a limited time to quantitative analysis concurrent with or following the usual qualitative course; it will be found also to be very useful as a book of reference to the general analytical chemist, who cannot be expected to have every method at his fingers' ends; though, owing to limitations of space, full details of every method cannot be given.

Part I. deals with the elementary principles of chemical analysis, such as sampling, weighing, and the various manipulative operations necessary to carry out a quantitative chemical analysis by the gravimetric method. This is followed by special sections giving the broad outlines and general methods in vogue for volumetric analysis, gasometry, and attributive methods, by which are meant certain methods based on other properties, common or special, besides weight and volume, or the measure of a chemical reaction, that stand in a definite relation to mass. Among these may be mentioned specific gravity, melting- and congealing-points, spectrum analysis, flash-points, &c.

Part II., which covers 51 pages, consists of a number of exercises in quantitative analysis of very varied kinds, such as cast-iron, ginger, potassium chlorate, chloral hydrate, nickel-copper alloy, air, &c.

Part III., which is the largest and most valuable portion of the book, is devoted to special methods and technical analysis, and includes the fire assay, colorimetry, electrolysis, ultimate and proximate organic analysis, the alkaloids, tannins, carbohydrates, oils, soaps, dye-stuffs, &c.

Part IV. contains notes and observations on the principles and practice of analysis, which may be useful to students, while the appendix contains certain observations on technical and industrial analysis, in which the great and growing value of the chemist cannot be over-estimated. There is a good index of ten columns.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 5, February 2, 1903.

Etherification of Mannite by Phosphoric Acid.—P. Carré.—Whilst repeating MM. Portes and Prunier's experiments on the etherification of mannite by phosphoric acid, the author observes the two following facts:—(1) Water is given off before the etherification starts, which seems to show that there is a dehydration of the mannite itself under the influence of phosphoric acid. (2) The velocity of etherification of the equimolecular mixture is much slower than is usually the case with the primary alcohols. In spite of numerous efforts, the author is not able to isolate in at all a pure state the salt of the di-ether formed with a prolonged heating action. In no case does he prove the formation of a non-salifiable ether, because in the various etherifications effected the whole of the acid used in the reaction can be recovered.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xxvii., No. 15.

Micrometric Assay of Gold Ores.—M. Gerreau.—Already inserted in full.

Pasty Condition assumed by Aluminium in the Neighbourhood of its Melting-point, and the Application of this Property to the Division of the Metal. —Albert Granger.—Already inserted in full.

Apparatus for the Examination of Contact Action. The Use of a Platinum Spiral.—A. Trillat.—To obtain good results in an apparatus with an incandescent platinum spiral, the contact action should be limited, and after the contact of the vapours examined, these should be cooled and isolated immediately. The platinum spiral must be arranged so that it can be raised to incandescence without heating the sides of the vessel containing it, and resistances must be arranged so that the temperature can be varied. The apparatus, of which a figure is given in the original, consists of a tube of thin glass of 10 to 15 c.m. long by about 8 m.m. diameter; this tube contains the platinum spiral. The lower part of this tube, which must be vertical, is fixed to a brass or silver tube of 6 m.m. outside diameter by means of an indiarubber tube; the upper end of the tube is fixed to a copper tube in the same manner. These two metallic tubes are connected by a spiral of platinum wire. The whole of this portion of the apparatus is placed in a glass cylinder 25 to 30 c.m. long by 8 wide, containing water, which serves to cool the vapours which have been in contact with the incandescent spiral. The substance to be examined is placed in a flask heated either directly or in a water-bath. The flask should have rather a long neck, and the cork must have two holes, through one of which passes a tube 7 or 8 m.m. diameter, bent at a right angle, and connected to the upper end of the copper tube. Through the other hole passes a tube reaching to the bottom of the flask. The lower end of the brass tube is connected with a flask of 100 or 200 c.c., closed with a cork having three holes through which tubes pass connected with various wash-bottles and reagent flasks. The flask itself is packed in ice. The vapour is drawn through the whole system by attaching the end to an exhaust pump or aspirator. The incandescence of the spiral is effected by means of an electric current and a rheostat for its regulation. The rest of the paper gives the precautions to be observed in carrying out the experiments.

Lactates of Mercury.— Marcel Guerbet.— Already inserted in full.

Sulphurised and Nitrated Derivatives of Sulphide of Carbon. V. Thiosulphocarbamic Derivatives of the Secondary Aromatic Amines. VI. Imidodithiocarbamic Aromatic Ethers. — Marcel Delépine. — Already noticed.

The Detection and Presence of Rennet in Plants.—Maurice Javillier.—Though much work has been done on the coagulation of milk with rennet, no one appears to have made experiments under sufficiently rigorous conditions. There are many microbes capable of coagulating milk, but no one appears to have sterilised the milk used in these experiments. The author has been working on strictly aseptic lines, and took rye-grass (*Lolium perenne, L.*) as the subject of his experiments. Rye-juice was prepared and saturated with chloroform and left for twenty-four hours in a stoppered flask in the dark; it was then filtered. Fifty drops of this juice were added to 10 c.c. of sterile milk, and a second tube of milk was treated with 50 drops of the juice, which had been boiled for fifteen minutes. The first tube was coagulated after three and a-half hours in the incubator at 38°. The second one was not coagulated at all. Thus rye-grass juice contains rennet, but rennet is destroyed on heating to 70—75°. Experiment showed that 45° is the optimal temperature for the action of this rennet. At low temperatures—such as 0°, 11°, and 16°—no coagulation takes place. Further experiments show that this rennet is influenced by dilution. Equal volumes of the filtered juice and sterile water coagulated milk in two hours, while a dilution of 4 parts of sterile water to one of juice took more than ten hours to coagulate milk. This rennet will act in neutral media, but its action is helped by acids and hindered by alkalis. The author gives, finally, a list of the plants in which he has found vegetable rennet; they number seventeen.

MISCELLANEOUS.

The Oxalo-uranous Salts. — V. Kohlschutter. — *Uranous oxalate*, $(C_2O_4)_2U+6H_2O$ (the author has doubled this formula in order to explain the composition of the following salts):—When $C_2O_4H_2$ is added to a solution of uranous chloride, a greyish precipitate is formed; its solution in oxalate of ammonium being poured into hydrochloric acid in a thin stream, the salt is re-precipitated in the form of green quadratic prisms.. *Acid Uranous Oxalate*, $2(C_2O_4)_2U.C_2O_4H_2+8H_2O$.—A nearly white precipitate is formed when we add a large excess of $C_2O_4H_2$ to UCl_4; water or dilute acids decompose it, giving the neutral salt, and this latter cannot be brought back to the state of acid salt by the addition of $C_2O_4H_2$. *Diuranous Chloro-trioxalate*, $(C_2O_4)_3Cl_2U_2+12H_2O$.—Five grms. of $(C_2O_4)_2U$ are heated with 60 grms. of concentrated HCl, the salt dissolves, and the solution is left to cool; it is not oxidisable in the air; when water is added it gives a white precipitate which contains all the uranium. When left in the desiccator with sulphuric acid for one or two days it forms small colourless flakes grouped together in tufts or spherical masses; at 100° this body loses first water, then HCl, and becomes rose-coloured. *Diuranous Sulphate-trioxalate*, $(C_2O_4)_3SO_4U_2+12H_2O$.—Five grms. of $(C_2O_4)_2U$ are dissolved in 75 c.c. of concentrated HCl, and after cooling, it is poured drop by drop into dilute sulphuric acid until a persistent cloudiness is formed. Soon a greenish-grey precipitate is formed consisting of very small needles; this salt is decomposed by water; with an excess of dilute sulphuric acid we obtain the following salt:—*Uranous Sulphate-oxalate*, $C_2O_4\ SO_4U+3H_2O$.—Three grms. of $(C_2O_4)_2U$ are boiled with 20—30 c.c. of dilute sulphuric acid; the salt becomes gradually deep olive-green coloured, and changes into small tabular prisms. This salt is insoluble in water and in dilute acids, neither is it decomposed by them; it is the most stable of the series. *Uranous Sulphate*, $(SO_4)_2U+4H_2O$.—Triturate $U(C_2O_4)_2$ with concentrated H_2SO_4, and pour the whole into alcohol; a slightly bluish white powder is deposited, free from oxalic acid. This salt dissolves in water at first, but is soon decomposed; it dissolves in dilute sulphuric acid, giving an oxidisable liquid, without doubt the acid sulphate; the addition of an excess of concentrated sulphuric acid precipitates small needles of neutral sulphate crystallised with $2H_2O$. On the other hand, if we let the solution of uranous sulphate in dilute sulphuric acid evaporate, we get dark green orthorhombic plates, isomorphous with sulphate of thorium, and of the same composition as the original bluish-white salt, but this new salt is insoluble in dilute sulphuric acid; the author regards it as a polymer with the double formula, $(SO_4)_4U_2+8H_2O$. The sulphuric solution of the original salt, treated with alkaline sulphates, gives the green, crystallised, double salts, $SO_4K_2.(SO_4)_2U+2H_2O$ and $4SO_4(NH_4)_2.(SO_4)_2U+3H_2O$. —*Double Uranous Oxalates.*—The solution of $(C_2O_4)_2U$ in $C_2O_4K_2$ on concentration and cooling, gives very soluble grey crystals, $2C_2O_4K_2(C_2O_4)_2U+5H_2O$, and these, on the addition of $BaCl_2$, give a violet-red, microcrystalline precipitate, $2C_2O_4Ba.(C_2O_4)_2U+6H_2O$. By evaporation in the cold we can obtain another uranosopotassic oxalate, $3C_2O_4K_2.(C_2O_4)_2U+4H_2O$, in green prisms; on boiling with water the latter gives $C_2O_4K_2(C_2O_4)_2U+8H_2O$, a greyish-white crystalline powder. *Chloro-oxalate of Thorium*, $(C_2O_4)_3Cl_2Th_2+9H_2O$. —Five grms. of $(C_2O_4)_2Th$ are dissolved at a gentle heat in 50 c.c. of concentrated hydrochloric acid; the solution, cooled and evaporated to dryness, deposits spherical tufts formed of plates of the chloro-oxalate; this salt is decomposed by water, and resembles the uranous salt. — *Berichte*, vol. xxxiv., p. 3619.

Exhibit of Irish Minerals and Building Stones at the Imperial Institute, London.—The Department of Agricultural and Technical Instruction for Ireland have taken steps to place on view for a period of three months at the Imperial Institute, London, the extensive collection of Irish minerals and building stones which formed one of the most interesting and valuable of their exhibits at the recent Exhibition in Cork. The exhibit will embrace samples of the varied and excellent building materials and marbles in which Ireland is particularly rich, and it is expected that the opportunity of examining these samples will be of advantage to those who are concerned in the many large building schemes now in progress in London and elsewhere in Great Britain. The beauty and excellence of the Irish granites, sand-stones, and limestones, as well as of the red, green, and black marble, and the other ornamental stones of the country, are well known, and when shown at the Department's Exhibit at Cork excited the admiration of all who saw them. The exhibit also includes specimens of clays, cement-making materials, and fine sands. In the mineral section of the exhibit are a series of prospectors' samples of the metalliferous deposits of the country, and samples of Irish coal and other minerals now being worked. The Mineral Expert to the department will remain with the exhibit during the period mentioned, and all inquiries should be addressed to E. St. John Lyburn, F.G.S., Irish Mineral Section, Imperial Institute, London, S.W. The Exhibition will be open free to the public from February 26th, 1903, between the hours of 11 and 5. Admission will be by the East Public Entrance of the Imperial Institute.

MEETINGS FOR THE WEEK.

MONDAY, March 2nd.—Society of Arts, 8. (Cantor Lectures). "Hertzian Wave Telegraphy in Theory and Practice," by Prof. J. A. Fleming, M.A., D.Sc., F.R.S.

—— Society of Chemical Industry, 8. "The need of Duty-free Alcohol for Industrial Purposes," by Thomas Tyrer, F.I.C., &c.

TUESDAY, 3rd.—Royal Institution, 5. "Recent Advances in Photographic Science," by Sir William Abney, K.C.B., D.C.L., F.R.S.

—— Society of Arts, 4.30. "The Uganda of To-day," by Herbert Samuel, M.P.

WEDNESDAY, 4th.—Society of Arts, 8. "Education in Holland," by J. C. Medd.

—— Society of Public Analysts, 8. "A Plea for the More Extended Consideration of Physics in Analytical Methods," by H. Droop Richmond, F.I.C. "Note on some Vanadium Reactions," by C. A. Mitchell, B.A., F.I.C. "Note on Adulterated Bees' Wax" and "The Solubility of certain Mineral Salts in Ether," by Otto Hehner, F.I.C.

THURSDAY, 5th.—Royal Institution, 5. "Insect Contrivances," by Prof. L. C. Miall, F.R.S.

—— Chemical, 8. "The mechanism of the Reduction of Potassium Bichromate by Sulphurous Acid," by H. Bassett. "The Constitution of Pilocarpine" (Part IV.), by H. A. D. Jowett. "Preparation and Properties of 1.4 (or 1.5) Dimethyl Glyoxaline and 1.3 Dimethyl Pyrazole," by H. A. D. Jowett and C. E. Potter. "Some Analyses of 'Reh,' or the Alkaline Salts in Indian Usar Land," by E. G. Hill. "Experiments on the Synthesis of Camphoric Acid—Part III., Synthesis of Isolauronolic Acid," by W. H. Perkin, jun., and J. F. Thorpe. "Camphor-β-thiol," by T. M. Lowry and G. C. Donington. "Isomeric Change of Dibenzanilide into Benzoylorthoamino- and Benzoylpara-aminobenzophenone," by F. D. Chattaway. "The Rate of Decomposition of Diazo-compounds—Part III., The Temperature Coefficient," by J. C. Cain and F. Nicoll.

FRIDAY, 6th.—Royal Institution, 9. "Studies in Experimental Phonetics," by Prof. J. G. McKendrick, F.R.S., &c.

SATURDAY, 7th.—Royal Institution, 3. "Light—its Origin and Nature," by Lord Rayleigh, F.R.S., &c.

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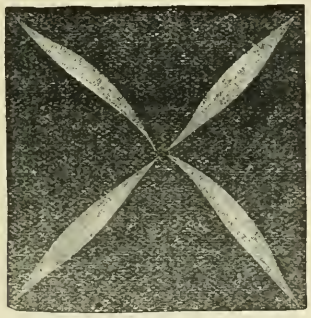
THE CHEMICAL NEWS.

Vol. LXXXVII., No. 2258.

ON THE FORMATION OF DEFINITE FIGURES BY THE DEPOSITION OF DUST.*

By W. J. RUSSELL, Ph.D., F.R.S.

The author shows that when a plate of glass or other material is slightly warmed and allowed to cool for six or seven minutes in a dust-laden atmosphere, a clear and definite figure is formed on the plate. The figure is determined by the form of the plate on which it is deposited. If a square plate is used then a simple cross is formed, a ray of deposit proceeds from each corner of the plate to the centre. If the plate be triangular, a ray again proceeds from each corner; and with an octangular plate an eight-rayed star is formed. In every case the number and position of the angles of the plate determine the form of the figure. The dust generally used was that produced by burning magnesium ribbon, but any fine dust acts in the same way and produces the same figures.



With regard to the plate on which the figure is deposited, its composition is not of importance except as a back-ground for the dust. A glass plate for many reasons is best, but the figures form with equal certainty and sharpness on one of copper, or mercury, or ebonite, or indiarubber, or card-board, &c. In order to heat the plate it may be passed several times over the flame of a lamp, warming it as uniformly as possible, and, if it be a glass plate, until the moisture condensed on the under side has disappeared; or the plate may be heated by laying it on a copper plate heated to about 120° C. for thirty minutes, or it may simply be warmed in an air- or water-bath. The plate is best supported on three pieces of wire about 1½ inches long, and a receiver filled with the dust, inverted over it and allowed to remain there for six or seven minutes.

In order to obtain symmetrical figures the plate on which they are deposited must be perfectly horizontal, and as they are very sensitive to heat, there must be no unequal heating either of the plate or the surrounding atmosphere while the deposition is taking place.

As long as the plate and the surrounding atmosphere are nearly of the same temperature only very imperfect figures form, but as the temperature rises a more and more nearly perfect figure appears. If the plate be above 17°, indications of pictures are produced when the plate is at a slightly lower temperature than the surrounding atmosphere, but when the difference is 6° or more, these indications cease altogether. Very good pictures are produced by having the plate at 12° or more degrees above the dust-laden air, and even when the plate is 100° or 120° above the air, distinct but thin pictures are produced. The effect of a slight heat below the plate, while the deposit is taking place, is shown to thicken the figure and distort it in a curious manner, and is illustrated by photographs. Also the effect of radiant heat on these figures is shown by the action of a Bunsen burner at distances of 12 and 26 inches, and of other sources of heat at considerable distances from the plate. Some singular and complicated effects are produced by placing a source of heat above the plate instead of below it. A large number of experiments are also recorded and illustrated showing the effect which different bodies in the immediate neighbourhood of the plate have on the figures which are formed. Taking only one case, that of a pin. When it is placed in contact and at right angles to the plate a definite deposit is produced, and this varies as the pin is moved further and further away, and as it is placed either on a level with plate, or above or below it. Even when the pin is 6 m.m. below the level of the plate, and 2 m.m. away from it, a distinct effect is produced. Again, these dust currents may be influenced in a remarkable way by suspending glasses of different sizes, and at different heights above the plate on which the figures are depositing, and photographs of the figures produced are given. The effects produced by obstructions of different sizes laid on different parts of the plate are also shown.

It was also found that a current of dust drawn through a tube will form a characteristic figure on a plate, which need not be warmed, as it passes over it.

If the magnesia dust be allowed to settle on a surface of water, about the temperature of 17° C. or, on water containing a very small amount of alcohol or glycerin, the deposit which forms on the surface breaks up, by the powder sinking, into a figure of cellular form.

Magnesia dust, which was generally used, undergoes some strange changes. When first deposited it is removed by the slightest touch, but if the plate be kept for a week or fortnight it may then be softly brushed over without damage to the figure. Another change which this powder undergoes is shown by collecting it immediately it forms, and examining it under a microscope, when it will be found to consist of irregular shaped and separate particles, but if the collection of the dust be made a few minutes after its formation, it is then seen that the particles are strung together, forming small and irregular fibres. In the various figures that have been produced the magnesia seems to have assumed this form.

* Abstract of a Paper read before the Royal Society, February 19th, 1903.

ESTIMATION OF THE FREE ANHYDROUS AND HYDRATED LIME IN CONCRETES.

By M. MAYNARD.

In January, 1897, during the course of some experiments in the laboratory at La Rochelle, we were led to try whether it would not be possible to estimate the free anhydrous or hydrated lime contained by all hydraulic products, no matter how carefully they have been manufactured.

Water acting on all concretes either to dissociate or to dissolve them, and acids of all kinds acting chemically on these products, it appeared impossible to estimate the free lime in them.

However, we can estimate this substance with sufficient approximation by having due regard to the following considerations:—

For this estimation it is necessary to find a body which does not contain any water which is able to dissolve lime without dissolving or dissociating the component parts of the cement, especially the aluminates and the tricalcic silicate. Now, chemically pure glycerin gives with lime a glycerinate of which the heat of formation is only 0·50 cal. : CaO + glycerin = glycerin . CaO + 0·50 cal.

Therefore by saponifying the cement with glycerin we ought to be able to dissolve the free lime only.

The first experiments were undertaken in December, 1898, on various products.

1. *Hydraulic Lime marked "Nivet," from Marans (Lower Charente).*—Three samples of 0·1 grm. of this lime were taken on December 8th, and each placed separately in contact with 50 c.c. of glycerin. On December 11th, one of these three samples were treated with 50 c.c. of absolute alcohol, and filtered on December 12th. A quantity of free lime was obtained equal to 35 per cent. On December 19th a second sample was treated with 40 c.c. of absolute alcohol, and filtered on December 20th; free lime equal to 34 per cent was obtained. On December 25th the third sample was treated with only 20 c.c. of absolute alcohol, and filtered on December 26th. The free lime obtained was equal to 28·52 per cent.

2 *Rapid Setting Cement, from Fumel (Dordogne).*—Unsifted cement, taken just as it came:—

On November 13th four assays were commenced on 1 grm. of cement, treated with 50 c.c. of glycerin.

On November 17th one sample was treated with 50 c.c. of absolute alcohol, and filtered on November 18th. The free lime = 5·33 per cent.

On November 23rd the second was treated with 50 c.c. of absolute alcohol, and filtered on the 24th. The free lime was 4·43 per cent.

On December 4th the next was treated with 50 c.c. of absolute alcohol, and filtered on December 5th. The free lime was 4·93 per cent.

On December 9th the last was treated with 50 c.c. of absolute alcohol, and filtered on December 10th. The free lime was 4·83 per cent.

Fine dust of cement passed through a silk sieve:—

On November 19th 1 grm. was placed in contact with 50 c.c. of glycerin, and on December 9th it was treated with 50 c.c. of absolute alcohol. The free lime found was 4·50 per cent.

On November 30th a sample of 0·5 grm. of cement was placed in contact with 50 c.c. glycerin; on December 7th 50 c.c. of absolute alcohol were added, and it was filtered on December 8th. The free lime found was 5·75 per cent.

3. *Cement marked Z, from Boulogne.*—The experiment was made in duplicate on November 20th and 30th, 1898. On November 20th 1 grm. of cement was put in contact with 50 c.c. of glycerin in four different flasks.

After 19 days we obtained 3·75 per cent of free lime.
" 23 " 3·29 " "
" 29 " 3·12 " "
" 35 " 3·20 " "

On November 30th 0·5 grm. of cement was put in contact with 50 c.c. of glycerin in three different flasks:—

After four days the amount of free lime obtained was 4·18 per cent; after nine days, 4·00 per cent; after twelve days, 4·21 per cent.

The variations between these two sets of results may be caused by the 50 c.c. of glycerin exhausting the free lime from the 0·5 grm. of cement more easily than from the 1 grm.

The first experiments were concluded by the estimation of the hydrated free lime contained in a block of Vicat maritime cement, of which we have spoken when referring to the action of sea-water on concretes, and which had been submerged since May 31st, 1859, at the foot of the Saint-Nicolas tower:—

The three assays made, gave:—

After 3 days contact, 2·62 per cent of free lime.
" 10 " 2·70 " "
" 14 " 2·34 " "
which gives a mean of 2·55 " "

The chemical composition of this product is rather variable, as can be seen from the analyses we give below:—

Moisture at 120°	22·30	23·40
Moisture between 120° and 180°	4·40	
Silica, soluble in alkalis	16·50	20·50
Silica, insoluble in alkalis	5·10	
Alumina	3·44	8·05
Peroxide of iron	2·55	2·75
Lime	32·64	31·00
Magnesia	3·69	3·04
Carbonic acid	7·44	9·50
Sulphuric acid	1·19	1·08
Chloride of sodium	0·65	0·60
	100·00	100·00

These first essays enable us to observe that glycerin was without action on the component parts of the cement, and that it was preferable, so as to prevent the agglutination of the cement, to add silica, and to give more fluidity to the glycerin to keep it at about 40°. Next we carried out a second series of experiments on a Portland cement mixed with and immersed in fresh water and salt water; this was analysed after varying periods of immersion. A cement marked "Couronne," from Boulogne was used.

For the estimations of the mixed and submerged cement, we made cubes of 0·06 metre of pure cement, of which one series was mixed with, and immersed in, fresh water, while the second was mixed with, and immersed in, sea-water.

These cubes were left untouched under water during the whole course of the trials, and the water was renewed every week. At fixed dates the cubes were withdrawn, dried at 120°, and broken up, and the samples for the estimation of the free lime taken from the interior in the centre of the blocks.

	Cement in powder.	Cement made with 23 per cent of fresh water and immersed in fresh water for—				
		24 hours.	30 days	3 months.	6 months.	1 year.
	P.c.	P.c.	P.c.	P.c	P.c.	P.c.
Silica	14·20	20·10	20·60	20·20	19·70	19·50
Alumina	15·90	9·19	8·00	6·08	7·59	11·25
Oxide of iron	2·50	2·01	2·50	2·72	2·01	2·55
Lime	65·15	61·90	62·89	62·48	55·74	51·70
Magnesia	0·14	0·10	0·12	traces	0·08	0·09
Sulphuric acid	0·75	0·80	0·45	0·68	0·82	1·24
Chloride of sodium	—	0·20	0·13	0·89	0·17	0·23
Loss from 120° to red heat	0·30	5·50	4·90	6·60	12·50	13·30
CO_2, and difference	1·06	0·20	0·41	0·35	0·55	0·15
Free lime on the cement dried at 120°	6·02	7·415	10·60	14·03	14·355	11·70

	Cement in powder.	Cement mixed with 23 per cent of sea-water and immersed in the same for—				
		24 hours.	30 days.	3 months.	6 months.	1 year.
Silica	14·20	20·50	20·60	20·00	19·60	19·00
Alumina	15·90	8·95	8·25	7·23	7·13	10·01
Oxide of iron	2·50	2·15	1·93	2·07	2·07	2·70
Lime	65·15	61·60	61·97	60·00	52·92	46·10
Magnesia	0·14	0·15	0·13	0·43	0·07	0·56
Sulphuric acid	0·75	0·89	0·85	0·82	1·05	4·28
Chloride of sodium	—	0·26	0·32	1·40	2·82	2·93
Loss from 120° to red heat	0·30	5·10	5·80	7·60	13·50	13·80
CO_2, and difference	1·06	0·40	0·15	0·45	0·74	0·78
Free lime on the cement dried at 120°	6·02	8·51	12·525	12·87	12·275	10·20

At the commencement of the estimations, after the period of contact with the cement was over, we diluted the glycerin with absolute alcohol which does not dissolve lime but facilitates the filtration of the solution. We em-

ployed another method also, which consists of heating the pure glycerin to 60° at the commencement of the filtration; this was effected by means of an apparatus with a continuous stream of warm water; at this temperature the surface tension of the glycerin is *nil*, and it is quite fluid.

The method of working is as follows:—

1. Weigh out accurately about 0·5 grm. of the cement under examination, and place it in a conical Erlenmeyer flask of about 150 c.c. capacity.

2. Raise 50 c.c. of pure glycerin to a temperature of 60°, and note exactly its volume in the graduated vessel holding it.

3. Pour the glycerin over the weighed cement, and close the neck of the flask with a plug of cotton-wool; shake for a few minutes, and place in an oven at 40°.

Care must be taken to note the volume of glycerin which remains in the graduated vessel, so as to know the exact volume of glycerin at 60° that was poured on to the cement.

Suppose, for example, that the volume of the glycerin used was 51 c.c. at the temperature of 60°, and the weight of the cement in contact with it 0·480 grm.

4. Leave the Erlenmeyer flask for five days in the oven, taking care to shake up the contents every day.

5. On the sixth day, filter the greater portion of the glycerin, taking care to keep the temperature up to about 60°.

We are of the opinion that this process will be very useful for observing the action of fresh water or of sea-water on submerged concretes. Thus we can follow the decomposition of mortars and verify their state of preservation.

We may remark that according to the results obtained we have never found proportions of 25, 30, and 44 per cent of free lime in Portland cements, as found by MM. Hart, Stener, Wermiser, and Spaujer.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 16.

THE ACTION OF CHROMIC ACID ON CARO'S REAGENT.

By A. BACH.

FOLLOWING on my experiments on the action of chromic acid on peroxide of hydrogen, I have examined the action of this oxidising agent on Caro's reagent.

We know that the product of the action of concentrated sulphuric acid on persulphate of potash does not act on chromic acid after its dilution with ice. On the other hand, I found that the undiluted product attacked chromic acid very vigorously either in the solid state or in sulphuric solution. There is a simultaneous reduction of the two bodies, with a liberation of oxygen and the formation of sulphate of chromium.

As I have shown in a previous paper (*Moniteur Scientifique*, 1901, p. 25), Caro's reagent behaves in quite an analogous manner with permanganate of potassium. In a dilute condition it has no action on the permanganate, but, on the other hand, when concentrated it reduces the solid permanganate or permanganic anhydride in sulphuric solution very energetically, with the liberation of oxygen and the formation of sulphate of manganese. In a large number of experiments I have noticed that the amount of oxygen given off in this case was almost exactly one-third more than the amount of reduced permanganic anhydride would have given off with peroxide of hydrogen. I have endeavoured to explain this fact by admitting that, under the influence of great concentration, 3 molecules of persulphuric acid combine to form a superoxygenated acid, analogous to tetroxide of potassium, and, like this latter, contain an ozonic group with a single atom of active oxygen.

The manner in which the product of the action of concentrated sulphuric acid on persulphate of potash behaves with chromic acid, enables us to test this hypothesis in another manner. If this product contained a superoxygenated acid of the type of tetroxide of potassium, it ought to give with chromic acid the same excess of oxygen as with permanganic anhydride. Experiments carried out for this purpose have shown, however, that undiluted Caro's reagent behaves exactly like peroxide of hydrogen with chromic acid; that is to say, that it reduces as much chromic acid and disengages as much oxygen as a solution of peroxide of hydrogen containing the same amount of active oxygen.

Exactly weighed quantities of persulphate of potash, of which the proportion of active oxygen present has been determined previously, were treated in the decomposing vessel of my apparatus with pure concentrated sulphuric acid, and, after the solution of the salt, the product was treated with an excess of chromic solution contained in the burette of the apparatus.

The chromic solution was prepared by dissolving pure chromic acid in pure concentrated sulphuric acid. Its proportion of available oxygen was determined iodometrically. The evolution of oxygen having ceased, the volume of gas liberated was read off on the graduated tube, and the green liquid resulting from the reaction was transferred to a test-glass with the help of 150 c.c. of water, and the unreduced chromic acid estimated therein. The following results were obtained in this manner:—

	Peroxide of hydrogen used.	Chromic oxygen in the reaction.	Oxygen given off.
	M.grms.	M.grms.	M grms.
	22·86	17 01	39·32
	25 04	18·22	43·41
	24 62	17·63	42·38
	22 25	16·21	39·02
Means..	23·69	17·26	41·03
Theory.	H_2O_2	17·77	41·46

We observe that the product of the action of concentrated sulphuric acid behaves, from the quantitative point of view with chromic acid, exactly the same as peroxide of hydrogen. Therefore the hypothesis of the presence of a superoxygenated acid in this product is no longer justified.

As a comparison, Caro's reagent, prepared from the same persulphate and the same sulphuric acid as above, was titrated with permanganic anhydride in sulphuric solution:—

Peroxide of hydrogen used.	Permanganic oxygen in the reaction.	Oxygen given off.
M.grms.	M grms.	M grms.
23·61	13·91	37·02
22 66	13·42	35·60
24 81	14·90	39·42
Means.. 23 66	14·09	37·34

With H_2O_2 the permanganic anhydride reduced should have given off .. .. 28·18 Oxygen

Excess of oxygen .. .. 9·16 „

Theoretical volume : volume found :: 1 : 1·32

Thus, the titration of undiluted Caro's reagent by means of permanganic anhydride has given again the same excess of oxygen as in the earlier experiments.

How can we explain the occurrence of this excess of oxygen?

The experiment with chromic acid having proved that it cannot be attributed to the presence of a superoxygenated acid containing more oxygen unstably combined than peroxide of hydrogen, we can only admit that the reaction between the permanganate and the peroxide takes a different course in sulphuric solution than in aqueous solution.

In this latter case, for each atom of available oxygen in the permanganate, 1 molecule of peroxide enters into the

reaction. If we take account of the excess of oxygen mentioned above, it seems probable that in sulphuric solution for each atom of available oxygen there is a reduction of $1\frac{2}{3}$ molecules of peroxide. From this it results that while the reaction in aqueous solution corresponds to the proportion,—

Permanganic oxygen : peroxide oxygen = 1 : 1,

the reaction in sulphuric solution takes place according to the proportion,—

Permanganic oxygen : peroxide oxygen = 3 : 5,

As to the chemical nature of Caro's reagent, it is certain that in the dilute condition it possesses other properties than in the undiluted state. In the first case, it does not react on permanganic, chromic, or titanic acids. In the second case, it attacks these reagents very energetically in the same manner as peroxide of hydrogen. It is not very probable that the presence of water is able to cause these differences of properties.—*Moniteur Scientifique*, February, 1903, Series 4, vol. xvii.

TETROXIDE OF HYDROGEN AND OZONIC ACID.

By A. BACH.

During my research on the slow oxidation of the nascent hydrogen given off by hydride of palladium (*Moniteur Scientifique*, 1897, p. 479), I observed a few analytical facts wh ch appear to be explained best by the hypothesis of the formation of a tetroxide of hydrogen. This tetroxide might result from the union of two incomplete groups, H.O.O. and O.O.H., and it ought to decompose according to the equation $H_2O_4 = O_3 + H_2O$, into ozone and water, and for this reason have a more energetic oxidising action than the binoxide of hydrogen.

Later on (*Moniteur Scientifique*, 1900, p, 424), I endeavoured to establish the existence of the tetroxide of hydrogen experimentally. By decomposing tetroxide of potassium by dilute sulphuric acid kept at a very low temperature, I obtained a very unstable solution of peroxide, which, when titrated with permanganate of potash, gave an excess of 30 to 50 per cent of oxygen, more than the amount of permanganate used ought to have given off with binoxide of hydrogen. In all probability I actually had here the hypothetical tetroxide of hydrogen that should be formed by tetroxide of potassium under the action of sulphuric acid, exactly as, for example, binoxide of sodium gives rise to the binoxide of hydrogen :—

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2.$$
$$K_2O_4 + H_2SO_4 = K_2SO_4 + H_2O_4.$$

Quite recently, Messrs. Baeyer and Villiger have published (*Berichte*, 1902, vol. xxxv., p. 3038) a note on "Ozonic Acid," which is very closely connected with the research I have just mentioned. By passing a current of ozonised oxygen over caustic potash in powder, they obtained an orange-brown product to which they gave the name ozonate of potash, and which they looked upon provisionally as identical with tetroxide of potassium. The same body also appears to be formed when we pass a current of ozonised oxygen through potash-lye kept at a very low temperature. The free "ozonic acid" corresponding to ozonate of potash would be, according to Messrs. Baeyer and Villiger, the hydrate of ozone, $O_3 + H_2O = O_4H_2$.

It is easily seen that Messrs. Baeyer and Villiger's ozonic acid is nothing else than the tetroxide of hydrogen which was the object of my research. In fact, like the binoxide of hydrogen, tetroxide of hydrogen ought to possess acid properties and form well-defined salts. Of these salts we know already tetroxide of potassium and tetroxide of rubidium. But it is probable that the product obtained by Messrs Baeyer and Villiger is not tetroxide of potassium—judging from its manner of formation—but a product of the addition of 1 molecule of caustic potash to 1 molecule of ozone; that is to say, the acid salt of tetroxide of hydrogen, $KOH + O_3 = KO_4H$.

If this supposition is confirmed, the analogy between the salts of binoxide of hydrogen and those of tetroxide of hydrogen would be complete.

H.O.O.H.	H.O.O.O.O.H.
Na.O.O.H.	K.O.O.O.O.H. (?)
Na.O.O.Na.	K.O.O.O.O.K.

From what has been said, it follows that the term "ozonic acid" must not be looked upon as synonymous with tetroxide of hydrogen.—*Moniteur Scientifique*, Series 4, vol. xvii., p. 106.

THE PREPARATION OF BENZOYL-ACETYL PEROXIDE AND ITS USE AS AN INTESTINAL ANTISEPTIC IN CHOLERA AND DYSENTRY.*

By PAUL C. FREER, M.D., Ph.D.

In a paper published in the *American Chemical Journal* (vol. xxvii., p. 163), a method was described of preparing benzoyl-acetyl peroxide in any desired quantity and chemically pure.

Bacteriological investigation with the solutions of this peroxide in water have shown it to be intensely active as a germicide. One part of the hydrolysed substance in 177 parts of water, and containing only 0 05 per cent of active oxygen, destroys all germs, including spores, almost instantly, and even at a dilution of 1 to 3000, vegetating germs are killed, as a rule, within one minute, but the spores require an appreciably longer time. On comparing these results with similar ones with hydrogen peroxide at 1 to 1000, and phenol at 5 per cent, it was shown that hydrogen peroxide, although it contained ten times as much active oxygen as the solution of benzoyl-acetyl peroxide, was by no means as effective, and the same may be said of phenol.

Experiments showed that solutions of benzoyl-acetyl peroxide as dilute as 1 part in 10,000 absolutely destroy the comma bacillus when it is placed in them in fairly large quantities on the loop of a platinum wire, and growth was prevented, or at least was extremely slow, when the dilution was 1 in 30,000.

It has been demonstrated by means of experiments on dogs that benzoyl-acetyl peroxide can be given internally with success and without damage, and therefore, theoretically, it should be of the greatest value as an intestinal antiseptic.

Chemically considered, benzoyl-acetyl peroxide may be regarded as hydrogen peroxide in which one half of the hydrogen has been substituted by the benzoyl group, and the other half by acetyl. It can be considered, therefore, as the benzoylester of aceto-peracid, or as the acetylester of benzo-peracid, and as such it is subject to hydrolysis or saponification. Experiments by the author and Mr. F. G. Novy showed that benzoyl-acetyl peroxide is in itself inert, and that its activity as an oxidising substance and as a germicide only appears after it has been subjected to hydrolysis by means of water. When the substance is hydrolysed, the reaction consists of the formation of aceto-peracid, which remains in solution, and dibenzoyl peroxide, which is precipitated as a crystalline insoluble powder, and which can be filtered from the clear solution. The germicidal effect of the solution therefore depends upon the presence of aceto-peracid, together with small quantities of benzo-peracid.

In giving capsules of solid benzoyl-acetyl peroxide, this same hydrolysis will take place in the intestines, and the

* Abridged from the "Report of the Bureau of Government Laboratories," Manila, 1902.

resulting germicidal aceto-peracid will have its local effect. Dibenzoyl peroxide has been proved to be practically inert, probably owing to the great difficulty with which it is hydrolysed.

An attempt having been made to obtain a shipment of benzoyl-acetyl peroxide in good condition from America, and having resulted in failure, an attempt was made to prepare it on the spot (in the Philippine Islands), and a shipment of 10 kilos. each of benzaldehyde and acetic anhydride was obtained from Germany.

It soon became apparent that oxidation took place more rapidly at room temperatures common in Manila than it did in the United States; the yield is, however, somewhat impaired, as a larger proportion of dibenzoyl peroxide appears to be produced in this climate than is the case in America, but, nevertheless, the results were sufficiently satisfactory to warrant the construction of a larger apparatus in which 3 kilos. at a time could be worked up by means of a forced current of air.

After complete oxidation the crude product is placed in large tubulated vessels, covered with petroleum ether, and allowed to stand overnight, by which means the larger portion goes into solution. The extracted peroxide and solvent are then tapped off at the bottom, fresh liquid added, and the operation repeated a second time. The united solutions are then carefully concentrated on a water-bath, the temperature of which must not exceed 80°, until about one-third has been distilled off, after which the vessels are placed in the cold room in an ice plant. Crystals of benzoyl-acetyl peroxide, contaminated with some dibenzoyl peroxide, gradually separate, and are eventually filtered off and dried; re-crystallisation from petroleum ether was resorted to subsequently in order to obtain the substance in a pure state. In all 2750 grms. of benzoyl-acetyl peroxide were obtained. At first the hospitals were supplied with double gelatin capsules containing 0·3 grm. of benzoyl-acetyl peroxide each, but later it was found expedient to substitute a somewhat smaller dose of 0·25 grm. to be given more frequently, the best results being finally obtained by the use of the latter, after coating with two layers of celloidin.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, February 18th, 1903.

Prof. J. Emerson Reynolds, Sc.D., F.R.S., President, in the Chair.

Mr. J. P. Millington was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Robert Gordon Bibby, New College, Oxford; Thomas Devine, M.B., C.M., 11, Spencer Place, Leeds; Archibald Louis Robinson, B.A., 40, Trinity College, Dublin; Montague White Stevens, 2, Richmond Place, London, S.W.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As President—Prof. Tilden, F.R.S., *vice* Prof. J. Emerson Reynolds, F.R.S.

As Treasurer—Dr. Horace T. Brown, F.R.S., *vice* Prof. Tilden, F.R.S.

As Secretary—Prof. Wynne, F.R.S., *vice* Prof. Dunstan, F.R.S.

As Vice Presidents—Prof. Dunstan, F.R.S., and Mr. David Howard, *vice* Prof. Divers, F.R.S., and Dr. Stevenson.

As Ordinary Members of Council—Dr. J. T. Hewitt, Dr. C. A. Kohn, Dr. E. J. Mills, F.R.S., and Dr. S. Ruhemann, *vice* Mr. H. B. Baker, F.R.S., Dr. Chattaway, Prof. Clowes, and Dr. Lewkowitsch.

Dr. Hewitt, Dr. Thorne, and Dr. Orton were appointed to audit the Society's accounts.

International Congress of Applied Chemistry.

By direction of the Council, the following letter was read announcing the formation of a Joint Organising Committee in this country in connection with the International Congress of Applied Chemistry which is to be held in Berlin next June.

Society of Chemical Industry,
Palace Chambers, 9, Bridge St, Westminster,
London, S.W., February 10th, 1903.

"*International Congress of Applied Chemistry, Berlin.*"

Dear Sir,—I am directed to inform you that at the conference held at this office on the 6th inst. and referred to in my letter of the 26th ult., the following resolutions were passed:—

1. That the delegates appointed by the Royal Society, Chemical Society, and Society of Chemical Industry, to represent these Societies at the International Congress of Applied Chemistry to be held in Berlin in June next, agree to form the joint Organising Committee contemplated in the letter of May 30th last from the President of the Organising Committee at Berlin.

2. That the Organising Committee so formed invites the co-operation of the other Learned and Industrial Societies in Great Britain, whose members are interested in Applied Chemistry.

3. That the President of the Society of Chemical Industry be requested to act as Chairman of this Organising Committee.

4. That Mr. C. G. Cresswell be requested to act as Secretary *pro tem.*

5. That a copy of these resolutions be communicated to Dr. Otto Witt, President of the Congress.

I remain, your obedient servant,
(Signed) Chas. G. Cresswell.

The Secretary, Chemical Society.

The following delegates have been appointed by the Council to represent the Chemical Society at the Congress:—Prof. Tilden, Prof. Dunstan, Prof. W. H. Perkin, jun., and Dr. A. Scott.

Fellows of the Society who propose to attend the Congress next June are requested to send their names to the Secretaries, so that they may be communicated to the Organising Committee in Berlin.

A ballot for the election of Fellows was held, when the following were subsequently declared duly elected:—Gilbert John Alderton; George Henry Appleyard; Edwin Bayles Atkinson; K Bhaduri, M.A.; William Bowen; Samuel Bradbury; George Thomas Branch; Hubert William Bywaters, Ph.D.; William Henry Cadman; John Castell-Evans; Arthur John Codling; Francis George Cousins; Benjamin Claxton Coyle; Cecil Henry Desch, Ph.D., D.Sc.; Archibald Sefton Elford, B.A.; Robert Crosbie Farmer, M.Sc., Ph.D.; Leonard King Hindmarsh, B.A.; Franklin Wise Howorth; Moung Tha Huyin, B.A.; Maurice Kemp-Welch, B.A.; Frederic Herbert Lees; Arthur Graham Leigh; Harry Percy Lewis; Percy George Mander, B.Sc.; Frederick O'Brien, M.Sc.; George Montague Prichard; Thomas Samuel, B.A.; Alfred H. Scholefield, B.A., B.Sc.; Samuel Edward Sibley; Alec Bowring Steven, B.Sc.; George Malcolm Thomson; Charles Tilburn; Stanley Tolson; Francis Digby Toyne; Duncan Turner; John Mello Wadmore, B.A.; Thomas Crosbie Walsh; David John Williams; Albert Wilmore; William Wade Yeomans; Andrew Young, M.A., B.Sc.

Of the following papers, those marked * were read:—

*24. "*The Molecular Re-arrangement of N-substituted Imino-ethers.*" By G. D. Lander.

The re-arrangement of the atomic grouping ·C(OR):N· into ·CO·NR· may be effected catalytically (Knorr and Wheeler) or by heating (Wislicenus), and both kinds of

isomerisation have been studied with some of the recently prepared N-substituted imino-ethers.

Alkyl iodides prove more useful in the catalytic re-arrangement than bromides or chlorides, and the isomer isation by means of iodides has been examined with the following imino-ethers:—N-phenylacetimino-methyl- and -ethyl, N-*o*-tolyl- and N-*p*-tolylacetimino-ethyl, N-phenyl-benzimino-methyl and -ethyl, N-*o*-tolyl- and N-*p*-tolyl-benzimino-methyl and -ethyl, N-methylbenzimino-methyl and -ethyl, N ethylbenzimino-methyl and -ethyl, and N-benzylbenz mino-methyl- and -ethyl.

Isomerisation occurs more readily with the methyl than with the ethyl compounds, the former, for the most part, undergoing re-arrangement at 100°, a temperature at which there is very little change with the latter. The ease of transformation also depends on the orientation of the aryl group attached to nitrogen, *p*-tolyl changing more easily than *o*-tolyl compounds.

The following substituted amides which result from the isomeric change do not appear to have been previously described:—*Benzmethyl-o-tolylamide* (m. p. 65—66°) crystallises in prisms from ether and light petroleum; *benzethyl-o-tolylamide* melts at 71—72°; *benzmethyl-p tolylamide* and *benzethyl-p-tolylamide* form prisms melting at 46—48° and 38—40° respectively; *benzmethylbenzylamide* and *benzethylbenzylamide* are liquids boiling respectively at 213—214° (11 m.m.) and 214—216° (12 m.m.).

The re-arrangement by heat occurs far less readily. N-phenylacetimino-methyl ether undergoes partial isomerisation on prolonged boiling, and considerable isomeric change of N-methylbenzimino-methyl ether was obtained after nine hours' heating at 250—270°. With N phenyl-benzimino-methyl ether (*Ber.*, 1900, xxxiii., 1470), less conclusive results were got. With ethyl-imino-ethers, the main change produced by prolonged heating is the elimination of ethylene and re-generation of the parent amide. It is therefore doubtful whether the isomerisation can be caused by simple heating.

Attention was drawn to the formation of ethyl paracyanoformate, $(CN\cdot CO_2Et)_x$, from diethyl imino oxalate, $HN{:}C(OEt)CO_2Et$, by loss of alcohol and subsequent polymerisation.

Discussion.

Dr. Orton asked whether Dr. Lander had brought about the isomeric change of an O-iminoether into the N-alkyl compound by use of an alkyl iodide, in which the alkyl group was not identical with the alkyl group of the imino-ether. If the first stage of the change is the formation of an additive product of the alkyl iodide and the iminoether, then, if sufficient quantity of the alkyl iodide be used, a N-alkyl derivative should be obtained, which would possess the alkyl group of the alkyl iodide, and not that originally present in the O-iminoether.

Dr. Lander, in reply, stated that he had performed an experiment in which the catalytic action of normal propyl iodide (1 mol.) on a methyliminoether had been found to yield chiefly substituted methylamide, the corresponding propyl compound being also produced, but to a less extent, the trace of methyl iodide first formed proving more effective than the relatively large amount of higher iodide also present.

*25. "*The Nature and Probable Mechanism of the Replacement of Metallic by Organic Radicles in Tautomeric Compounds.*" By G. D. Lander.

The results of the alkylation of keto-enolic compounds and substituted amides by means of dry silver oxide and alkyl iodides (*Trans.*, 1900, lxxvii., 729); 1901, lxxix., 690; 1902, lxxxi., 591; *Proc.*, 1901, xvii, 59) were discussed in the light of the addition hypothesis and its modifications, and also with reference to the views on the mechanism of the replacement of metallic radicles in tautomeric compounds as developed by Wislicenus ("Tautomerie," *Ahrens-Sammlung*, 1897, 249). The opinion was advanced that none of these hypotheses is competent to give a perfectly general elucidation of the phenomena, and an explanation was therefore sought in the hypothesis of the display of tautomeric relationships by the compounds containing metallic radicles.

In order to test the validity of silver oxide alkylation as a basis for the discussion of the mechanism of this replacement of metallic radicles, the alkylation of ethyl oxaloacetate and formophenylamide by this method was investigated. The former yields ethyl ethoxyfumarate on treatment with silver oxide and ethyl iodide, a result agreeing with that obtained by Nef (*Annalen*, 1893, cclxxvii., 73); the latter, on methylation with silver oxide, gives chiefly N-phenylformiminomethyl ether, NPh:CH·OMe, together with small amounts of formophenylmethylamide, CHO·NMePh, and diphenylformamidine. The production of the last two substances does not appear to have been noted in the methylation of silver formophenylamide by Comstock and Kleeberg (*Am. Chem. Journ.*, 1891, xiii., 514), but a control experiment showed that both are formed in their process to a somewhat greater extent than by the silver oxide methylation.

Methylation of the substituted amides by means of silver oxide leads to the formation of mixtures of imino-ethers and isomeric substituted amides, ethylation of these amides under similar conditions apparently gives rise exclusively to imino-ethers. When, however, the ethylation of acetophenylamide by means of silver oxide is conducted in a closed vessel at 100°, N-phenylacetimino-ethyl ether, NPh:CMe·OEt, and the isomeric amide, NEtPh·CMeO, are both produced, just as isomerides are formed in the methylation of the same amide in open vessels at the ordinary temperature or at 40—50°.

N-phenylbenziminomethyl ether, NPh:CPh·OMe, does not undergo isomeric change when boiled in benzene solution for four hours with dry silver oxide and methyl iodide.

*26. "*The Chlorine Derivatives of Pyridine.* Part VIII. *The Interaction of 2 : 3 : 4 : 5-Tetrachloropyridine with Ethyl Sodiomalonate.*" By W. J. Sell and F. W. Dootson.

The chief product of the interaction of 2 : 3 : 4 : 5-tetrachloropyridine and ethyl sodiomalonate is ethyl 2 : 3 : 5-trichloropyridyl-4-malonate, which, on hydrolysis, loses carbon dioxide, yielding 2 : 3 : 5-trichloropyridyl-4 acetic acid. The latter compound is non-volatile, and when heated a little beyond its melting-point, is quantitatively decomposed into 2 : 3 : 5-trichloro-4-methylpyridine and carbon dioxide. On oxidation with potassium permanganate, 2 : 3 : 5-trichloro 4-methylpyridine yields the corresponding acid. These changes may be thus represented:—

$$C_5NHCl_3\cdot CH(CO_2Et)_2 \rightarrow C_5NHCl_3\cdot CH_2\cdot CO_2Et \rightarrow C_5NHCl_3\cdot Me \rightarrow C_5NHCl_3\cdot CO_2H.$$

*27. "*The Biological Method for Resolving Inactive Acids into their Optically Active Components.*" By A. McKenzie and A. Harden.

In much of the research in this field, no attempt has been made to work with pure cultures. Hence, although the optically active products desired in certain cases were successfully obtained, there is often doubt as to the exact organism by which the resolution had actually been effected, the object having been to obtain the pure active isomeride rather than to examine the action of any particular organism on the inactive acid, and therefore many resolutions ascribed to *Penicillium glaucum* have probably been accomplished, not by that mould, but by bacteria with which the solution under investigation had accidentally become contaminated (compare Landolt, "Das Optische Drehungsvermögen," 1898, 63).

The authors have investigated the action of *Penicillium glaucum*, Link; *Sterigmatocystis nigra*, van Tieghem (= *Aspergillus niger*, van Tieghem, *olim*); and *Aspergillus griseus*, Link, and their action on racemic, dimethoxy-succinic, lactic, α-ethoxypropionic, α-propoxypropionic, α-hydroxybutyric, β-hydroxybutyric, glyceric, malic, methoxysuccinic, ethoxysuccinic, propoxysuccinic, man-

delic, methoxyphenylacetic, ethoxyphenylacetic, propoxyphenylacetic, α-bromopropionic, α-bromobutyric, chlorophenylacetic, and monobromosuccinic acids and alanine were investigated.

Their experiments tend to show that the mode of action of the moulds is such that the one active isomeride is attacked more readily than the other, and that the extent of the resolution depends solely on the difference of this rate of attack. The view generally held, namely, that the one isomeride is attacked whilst the other remains untouched, does not appear to be correct. Two other points were kept in view: firstly, whether, from the action of organisms, any definite relationship could be established as to the configuration of the various related acids; and, secondly, whether the active products of the action of different organisms on the same series of acids show any regularity as to sign of rotation.

28. "*Colour Changes observed in Solutions of Cobalt Chloride.*" By W. N. Hartley.

A paper by Donnan and Bassett (*Trans.*, 1902, lxxxi, 939) contains a reference to some work on the action of heat on the absorption spectra and chemical constitution of saline solutions, and to this (*Sci. Trans. Roy. Dublin Soc.*, 1900 [7], 253) the author takes exception, as being misleading in certain important particulars.

The characteristic spectra of aqueous solutions of cobalt chloride saturated at 20°, as seen in wedge-shaped cells at temperatures between 23° and 93°, differ from those of the hydrochloric acid solution; the compound formed at 93—100° in neutral solutions seems to be the dihydrate, $CoCl_2,2H_2O$, and not the anhydrous salt.

The solution in hydrochloric acid probably contains a compound of the salt with the acid, for the spectrum is peculiar; and, moreover, the anhydrous salt, which is insoluble in dry ether, dissolves in this medium when the mixture is treated with carefully dried hydrogen chloride.

Pure cobalt sulphate may be heated to 300° without perceptible change, and does not alter at a temperature approaching 800°.

Zinc chloride added to a solution of cobalt chloride prevents the development of the blue colouration on warming; this action may be explained by assuming the formation of a double chloride which does not give rise to the dihydrate. The changes produced by mercuric chloride on an alcoholic solution of cobalt chloride are due to the formation of the double cobalt mercuric chloride (Claudet's salt), a substance which in the solid state is particularly sensitive to changes of temperature. If the blue solution observed by Donnan and Bassett during the electrolysis of cobalt chloride is due to the formation at the anode of a complex ion, it should be possible to separate and analyse solutions containing these ions, and so determine the ratio of cobalt to chlorine.

The hypothesis that hydrated salts can exist in highly concentrated solutions, and can undergo dissociation on raising the temperature, accounts precisely for the phenomena observed not only in the case of cobalt chloride, but also in that of its iodide, bromide, and the salts of other metals.

29. "*The Action of Ammonia and Organic Bases on Ethyl Esters of Olefinedicarboxylic and Olefine-β-ketocarboxylic Acids.*" By S. Ruhemann.

Ethyl benzylidenemalonate condenses with benzamidine to form *ethyl dihydrodiphenylpyrimidonecarboxylate* (m. p. 188°) according to the equation—

$$CHPh:C(CO_2Et)_2+CPh(NH_2):NH=$$
$$=CHPh<\begin{matrix}CH(CO_2Et)\cdot CO\\ NH\text{ ——— }CPh\end{matrix}>N+C_2H_6O.$$

When this compound is treated with ammonia, the ring opens and then closes, with the loss of carbon dioxide and alcohol, forming *dihydrodiphenylpyrimidone* (m. p. 180°), $CHPh<\begin{matrix}CH_2—CO\\ NH\cdot CPh\end{matrix}>N$, which is also formed by the action of benzamidine on ethyl benzylideneacetoacetate in accordance with the following equation:—

$$CH_3\cdot CO\cdot C(CO_2Et):CHPh+CPh(NH_2):NH+C_2H_6O=$$
$$=CH_2<\begin{matrix}CO_2Et\quad NH\\ CHPh—NH\end{matrix}>CPh+CH_3\cdot CO_2Et=$$
$$=CH_2<\begin{matrix}CO\text{ ——— }N\\ CHPh\cdot NH\end{matrix}>CPh+CH_3\cdot CO_2Et+C_2H_6O.$$

In studying the action of ammonia on ethyl esters of olefine-β ketocarboxylic acids, it was found that both ethyl ethylideneacetoacetate and ethyl furylideneacetoacetate are transformed by ammonia into ethyl hydrocollidinedicarboxylate and ethyl hydrofuryllutidenedicarboxylate respectively. The formation of these compounds depends on the previous decomposition of the ethyl olefine-β-ketocarboxylic ester into ethyl acetoacetate and the aldehyde ammonias, which, in turn, condense to form the hydrogenised pyridine derivatives.

Ethyl benzylideneacetoacetate,—

$$CH_3\cdot CO\cdot C(CO_2Et):CHPh,$$

behaves differently towards ammonia, and yields *benzylideneaminoacetone*, $CH_3\cdot CO\cdot C(NH_2):CH\cdot C_6H_5$ (colourless needles, m. p. 125°). This substance, on heating with acids, readily loses benzaldehyde. On carefully warming the ketone with concentrated hydrochloric acid, an insoluble chloride is produced which may be regarded as diacetobenzylideneimide hydrochloride, $NH(CAc:CHPh)_2,HCl$.

30. "*Derivatives of* p *Aminoacetophenone.*" By F. D. Chattaway.

In the course of a study of the transformation of diacetanilide into aceto-*p*-aminoacetophenone under the influence of hydrogen chloride or of zinc chloride, the following compounds have been prepared. They are formed by the ordinary processes, but in the preparation of the nitrogen-halogen derivatives great care must be taken to avoid the liberation of free halogen, otherwise substitution in the ketonic chain occurs.

p - *Acetylchloroaminoacetophenone*, $C_6H_4Ac\cdot NAcCl$, colourless, pearly plates, readily soluble in chloroform, m. p. 72°; p-*acetylbromoaminoacetophenone*, $C_6H_4Ac\cdot NAcBr$, yellow, rhombic plates, m. p. 83°; p-*propionylaminoacetophenone*, $C_6H_4Ac\cdot NH\cdot COEt$, colourless prisms, m. p. 136°; p-*propionylchloroaminoacetophenone*, $C_6H_4Ac\cdot N(COEt)Cl$, colourless plates, m. p. 42°; p-*benzoylaminoacetophenone*, $C_6H_4Ac\cdot NH\cdot COPh$, thin colourless plates, m. p. 205°; p-*benzoylchloroaminoacetophenone*, $C_6H_4Ac\cdot N(COPh)Cl$, colourless plates, m. p. 77°.

On heating, the nitrogen-halogen derivatives undergo transformation with considerable decomposition; when dissolved and warmed in acetic acid, halogen passes from the nitrogen into the ortho-position in the nucleus, whilst, if free halogen is liberated, substitution in the methyl group of the ketone also takes place.

Anniversary Dinner.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Whitehall Rooms, Hotel Métropole, at 6.30 for 7 o'clock, on Wednesday, March 25th, 1903 (the day fixed for the Annual General Meeting).

PHYSICAL SOCIETY.

Ordinary Meeting, February 27th, 1903.

Dr. R. T. Glazebrook, F.R.S., President, in the Chair.

A paper by Prof. Fleming and Mr. Clinton "*On the Measurement of Small Capacities and Inductances*" was read by Prof. Fleming.

The measurement of small capacities and inductances has become important in connection with Hertzian Wave Wireless Telegraphy. For the measurement of small capacities, when the dielectric is air or some other sub-

stance not possessing the quality commonly called absorption, no method is so easy to apply as that depending upon the rapid charge and discharge of a condenser through a galvanometer. This method has been extensively employed, the only difference being in the nature of the commutator for charging and discharging the condenser. The authors of the paper have had considerable experience with tuning-fork devices for commutating, but have found them troublesome in practice. They have therefore designed a rotating commutator which renders the measurement of small capacities a matter as easy as the measurement of resistance on a Wheatstone bridge. The appliance is described in the paper, and the authors claim that they have worked out a thoroughly satisfactory form of rotating commutator, designed more from the point of view of an engineer than an electrical instrument maker. For use with the instrument a moving-coil differential galvanometer has been designed. The magnetic field at either of the coils can be varied by means of a piece of soft iron which can be moved about in the field. By using a differential galvanometer the method can be reduced to a null one and made independent of a knowledge of the E.M.F. employed in the experiments. The authors have made a number of experiments upon the capacity of aërial wires, such as are used in Hertzian Wave Telegraphy, and have also investigated the laws governing the capacity of such wires when grouped together in certain ways, and verified experimentally, as far as possible, the formulæ for the capacity of insulated wires in various positions in regard to the earth. The experiments are given at length in the paper, and the results practically obtained are compared with those derived from theoretical considerations. In all cases the total measured capacity of n wires is less than n times the capacity of one wire. In dealing with small capacities a difficulty arises in connection with the allowance to be made for the capacities of the leads and the commutator. The capacity of an object measured, as it would be in free space, is only obtained to a first approximation by deducting the capacity of the leading wire and commutator from that of the leading wire, commutator, and object. For the measurement of small inductances the authors have constructed an instrument, similar to the secohmmeter of Ayrton and Perry, upon the same lines as their rotating commutator. By making the apparatus substantial and eliminating all insulating material, except air, from the surface of the rotating drums, and abolishing all flimsy spring contacts, they have produced an apparatus which is much more satisfactory to work with than the ordinary secohmmeter of the instrument-makers. The determinations of inductance were made by Anderson's method.

Prof. AYRTON said he was glad to see that the authors had brought out an apparatus constructed on engineering lines. He mentioned that the secohmmeter used in his laboratory was not the instrument of the instrument-makers' catalogues, but more like the one exhibited. Prof. Fleming had given some account of the history of the subject, and had referred to early experiments carried out by using tuning-forks as commutators. Rotating commutators were, however, in use some time before the introduction of tuning-fork arrangements. The fact that air was superior to mica, ebonite, or other substances as the insulating material at the surface of a rotating commutator had been recognised by Prof. Perry and himself in a patent taken out many years ago. The authors had raised the question of the legitimacy of subtracting the measured capacity of the commutator and leads from the measured capacity of the commutator, leads, and condenser in order to obtain the capacity of the condenser. He pointed out that the results of the experiments described in the paper showed that this procedure was wrong. He asked in what respect Anderson's method of measuring a self-induction was superior to the method of comparing it directly with a standard variable self-induction. Referring to the galvanometer used in the experiments, Prof. Ayrton pointed out that the device of shunting the magnetic flux through a piece of soft iron had been used before. There were two objects in employing such a shunt. In the first case, when using an ordinary moving-coil galvanometer as a voltmeter, it was necessary to keep the sensibility constant, and any alteration in the strength of the magnets could be counterbalanced by a movement of the shunt. In the second case, the shunt was useful in the construction of differential moving-coil galvanometers. Some years ago a series of observations were conducted in his laboratory to determine the errors which might enter into experiments carried out with a rotating commutator, and he remarked that, in order to avoid contact differences of potential, it was essential that the commutator and the brushes should be made of the same material.

Prof. S. P. THOMPSON said the experiments were the first which had been made upon the capacities of wires suspended near each other in air. Referring to the measurement of small capacities Prof. Thompson briefly described a method which he had published similar to Carey Foster's method of comparing two nearly equal resistances. All that is required for accuracy is a known standard capacity and a calibrated sliding condenser.

Mr. A. CAMPBELL exhibited the commutator used for condenser tests at the National Physical Laboratory. It is similar to that designed by Mr. Searle and used by him and Prof. J. J. Thomson in their determination of the value of "v." In this commutator the ebonite insulation does not fill the spaces between the segments, and is never touched by the brushes, thus giving satisfactory insulation. By its aid many measurements have been made of the B.A. air-condensers, the capacity of each of these being about 0·02 m.fd. The galvanometer used was so sensitive that the time-measurement had to be carefully performed to get equal accuracy. In the earlier experiments an ordinary moving-magnet galvanometer was used, but it was discovered that if the magnet at its zero position was not exactly parallel to the planes of the coils, considerable changes occurred in the observed capacities when the battery was reversed. This effect was due to the fact that, with the needle in such a position, the galvanometer could respond to alternating currents, and that its deflection (except when the needle was exactly at right angles to the coil axis) was partly due to the mean current and partly to the square-root mean-square current. When a condenser of $\frac{1}{3}$ m.fd. was put in parallel with the galvanometer the effect practically disappeared. A moving coil galvanometer, however, was found to be quite free from such effects, and this type had been used in nearly all the tests. The differential galvanometer described by the authors appeared admirable, and would be a useful instrument for a number of purposes, a great advantage being that the mutual inductance from coil to coil would be very small.

Mr. JACOB asked Mr. Campbell if he was sure that the movement of the galvanometer-needle mentioned by him was not due to electrostatic effects. He pointed out that if a differential moving coil-galvanometer was correctly balanced for one point of the scale, it did not follow that it would remain balanced at any other point. It was a matter of common knowledge that the total capacity of wires near each other was less than the sum of the capacities of the wires taken separately.

Mr. J. T. MORRIS asked if the authors had any proof that the condenser was perfectly charged and discharged on every occasion. He drew attention to the fact that the capacity might depend upon the form of the wave of potential difference which charged it.

Mr. R. APPLEYARD said that the capacity of a condenser with mica dielectric determined from a single charge and discharge was practically the same as that obtained from several charges and discharges per second. This was not the case with rubber. He asked if the authors had observed differences in capacity depending upon the point of attachment of the leading wire.

Mr. W. C. CLINTON, in reply, said they had used

Anderson's method because they found it more convenient than any other. It required no arbitrary standard of inductance or determination of speed, the only things required being resistance-boxes and a known capacity. They had obtained different capacities for wires by varying the point of attachment of the lead, the maximum variation amounting to about 5 per cent of the total capacity.

A paper "*On the Thickness of the Liquid Film formed by Condensation at the Surface of a Solid*," was read by Dr. G. J. Parks.

It was known more than half a century ago that when a solid is placed in a gas or vapour there is a condensation of the latter on the surface of the solid, and in particular that glass has the power of condensing water-vapour at temperatures above the dew-point. In order to determine the thickness of the liquid film, the author has exposed masses of cotton-silicate of known area to the action of water-vapour. From the increase in weight he has calculated that the thickness of the film is $13{\cdot}4 \times 10^{-6}$ cms. The cotton-silicate thus covered with a film of moisture showed no alteration in appearance even when examined under the highest power of the microscope, but when the silicate was placed in water, no heat was evolved. It may therefore be inferred that the Pouillet effect for water in contact with glass at about 12° C. is confined to a film of moisture, the thickness of which is about $13{\cdot}4 \times 10^{-6}$ cms. The Author has compared his results with those obtained by other experimenters with different substances and under widely different conditions, and concludes that in all cases where condensation of moisture takes place at a solid surface, and at temperatures not below the dew-point, the thickness of the surface-film varies from 10×10^{-6} to 80×10^{-6} cms., according to the substances used and the conditions of temperature and pressure.

Prof. Everett remarked that similar experiments upon different kinds of glass had been carried out by Kohlrausch. The glass, in the form of powder, was placed in a platinum dish under a bell-jar exposed to water vapour. The increases in weight varied from 2 per cent to 18 per cent, whereas the increase observed by Dr. Parks was only 1·2 per cent.

Prof. S. P. Thompson congratulated the Author upon the results of his experiments, but advised him to be cautious in using them in any attempt to determine the law of molecular attraction. Similar experiments were carried out in Bunsen's laboratory about twenty years ago.

Dr. J. A. Harker said that the liquid film on the surface of glass or porcelain was often a source of trouble in high temperature gas thermometry. He had found that in exhausting Röntgen-ray tubes it was apparently possible to get a complete vacuum at about 300° C., but on heating to a slightly higher temperature gases were given off from the walls of the tubes.

Mr. J. Brown, in a communication to the Secretary, stated that the paper recalled an investigation of his own undertaken with quite a different object, viz., the question as to whether the condensed films on plates of copper and zinc could be brought into contact so as to form the electrolyte of a voltaic cell and produce a current. The limit of separation of the plates at which the current ceased was measured very roughly, and came out considerably greater than that observed by Dr. Parks. It may be possible that the electrically conducting film has a much less specific gravity than ordinary water.

Dr. P. E. Shaw, in a communication to the Secretary, stated that in the Author's experiments, and in most of those referred to, the radius of curvature of the solid surface was small, and was in fact comparable with the thickness of the film deposited on it. It would be interesting to try the effect on flat surfaces, and also at temperatures below 0° C. He had observed the film on fine wires, which, brought into contact crossing at right angles, adhere with the force of the order of a dyne. Dr. Shaw had used the Author's value for the thickness of the film to explain the results obtained in 1901 by Mr. Earhart on the voltages required for sparking between surfaces when the distance between them is small. The dust particles in air have an enclosing film thick enough to contain and foster any of the well known bacilli.

The Chairman said the results were of particular interest to him, because he was at present engaged in making mercury standards of resistance. In his experiments it was necessary to measure the radii of the tubes with an accuracy comparable with the thickness of the liquid film.

Dr. Parks, in reply to Dr. Harker, said that powdered silica might be heated to 300°, and appear quite dry. On heating it slightly higher, however, large numbers of bubbles were given off suddenly, and the powder resembled a boiling liquid.

NOTICES OF BOOKS.

The Principles of Animal Nutrition; with Special Reference to the Nutrition of Farm Animals. By Henry Prentiss Armsby. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. Pp. viii.-614. 8vo.

This scholarly work is the product of one whose training and experience have well qualified him for its preparation. Dr. Armsby is well known as the Director of the Pennsylvania State College Agricultural Experiment Station, as well as Expert in Animal Nutrition, United States Department of Agriculture. The substance of the volume was given in the form of lectures before the Graduate Summer School of Agriculture at the Ohio State University in 1902.

Activity in the study of the problems of animal nutrition during the last quarter of a century has resulted in regarding these problems from a new point of view; to more accurate knowledge of the chemistry of nutrition has been added "a clear and fairly definite general conception of the vital activities as transformations of energy and of the food as essentially the vehicle for supplying that energy to the organism."

This volume presents in systematic form the fundamental principles of animal nutrition from the modern standpoint of energy relations, with special reference to farm animals; it is therefore on a higher plan than a mere treatise upon stock-feeding. Part I. deals with the income and expenditure of matter, in six chapters, the Food, Metabolism in its many phases, and its relation to food supply, and as affected by muscular exertion. Part II. treats of the income and expenditure of energy in thirteen well-studied chapters, the whole forming a compendium of great value and interest. No earnest student of the topics discussed in the pages of Dr. Armsby's work can afford to ignore it.

Many footnotes give the sources of the statements made in the text, but the reviewer regrets that the author in referring to periodicals has failed to add to the volume number, the date of issue; the value of a citation may often be weighed by knowing its date, an item which the reader cannot, as a rule, take time to supply.

The book is well made and printed; it has an uncommonly full index. It is pleasant to handle a new book that opens and lies flat. H.C.B.

The Chemistry of Indiarubber; Including the Outlines of a Theory on Vulcanisation. By Carl Otto Weber, Ph.D. With Four Plates and several Illustrations in the Text. London: Charles Griffin and Co., Ltd. 1902. Pp. 314.

The analysis of indiarubber was very little understood ten years ago; in fact, most of the work in this direction

has been done during the last decade. But as a mere compilation of analytical methods would have been only of technical interest, the author has wisely decided to extend the scope originally intended for this volume, and has written an important chapter on the "Chemistry of Indiarubber"; this forms Chapter I., and covers 115 pages.

Indiarubber, as is well known, is the product of the coagulation of the milky juices of a large number of trees, comparable to the oils, and more especially to the terpenes. Certain sugars, such as inosite, bornesite, and matezite, are present in indiarubber, and can be removed by washing with water. After washing and drying, the substance left forms technically pure rubber, but it is by no means chemically pure, as several oily and resinous substances can be extracted by means of certain solvents, such as alcohol or acetone. The elementary composition of indiarubber has been found by several authorities to be $C_{10}H_{16}$, and this is now generally taken to be correct, although Henriques has pointed out within recent years the possibility that indiarubber might be after all an oxygen compound.

Indiarubber in the highest state of chemical purity is a practically colourless substance, and its physical properties are of considerable interest; its distensibility increases considerably with an increase of temperature, and on cooling down to the temperature of liquid air Professor Dewar showed recently at the Royal Institution that even a thin sheet of rubber becomes sufficiently hard and rigid to withstand the pressure of a Torricellian vacuum, though it is at the same time exceedingly brittle.

Chapter III., on the examination of rubber substitutes, as well as the five following ones, is of technical interest, These chapters deal with "Inorganic Compounding Materials," "Vulcanisers and Sulphur Carriers," "Indiarubber Solvents," "Colouring Matters," and "The Constructive Components of Indiarubber Articles."

Chapter IX. is an important one, on the analysis of indiarubber articles; in it are enumerated physical, mechanical, and electrical tests; the chemical analysis of rubber, and analytical methods. The analysis of hard rubber goods, such as ebonite, is also dealt with; while the interpretation of results receives due attention.

There is an appendix on sanitary conditions in indiarubber works, a subject index, and one for authors' names.

This volume is a valuable contribution to the rather scanty scientific literature of indiarubber, and as it points out in what directions researches should be made, and where improvements are likely to be possible, it should be of much service to manufacturers and others connected with the indiarubber industry.

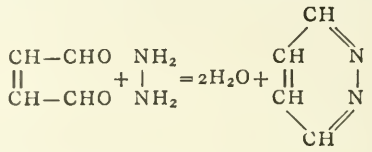
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 6, February 9, 1903.

The Displacement of the Sulphuric Acid in the Alkaline Bisulphates by Water.—Albert Colson.—The temperature at which the dilution of a body takes place without variation of temperature is a means of finding out whether an addition of water to a salt solution provokes chemical change. Solutions are taken containing—(1) 142 grms. of neutral sodium sulphate (Na_2SO_4) dissolved in a litre of normal sulphuric acid; (2) the same, diluted with its own volume of water; (3) a solution of one part of potassium bisulphate, $KHSO_4$, and four parts of water; and (4) the last, diluted with its own volume of water. An investigation of these four solutions leads the author to the conclusion that there is a possibility of extracting by the simple action of water a part of the acid from a salt, and utilising this acid for industrial purposes.

A New Synthesis of Orthodiazine.—R. Marquis.—Fumaric or maleic aldehyde should react on hydrazine, giving a cyclic compound containing 2 atoms of nitrogen—the compound orthodiazine, which is already known,—

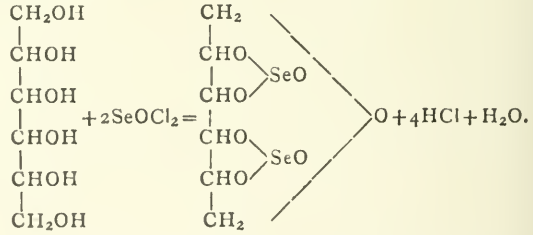


The author's experiments prove that this reaction does take place.

Formation of Azoic Compounds. Reduction of Orthonitrobenzylic Alcohol. — P. Freundler. — The author's experiments show that the reduction of orthonitrobenzylic alcohol takes place in quite a special manner. Using the minimum quantity of red acid, the composition of which is not at all certain, products formed during the normal reaction are not produced—such as azoic, hydrazoic, or azoxyic acids. All the bodies which are formed result from the transformation of the nitrated portion of the amine group, by oxidation of the alcoholic part of the aldehydic and acid function, and from condensation of a certain number of primary products with one another—a condensation which gives rise to more complex bodies.

Oxidation of Cobalt and Manganese Acetates by Chlorine.— H. Copaux.— The author finds that the acetates of cobalt and manganese are oxidised by chlorine in different ways. In the first case, a complex chloroacetic compound of the intermediate oxides Co_3O_4 is formed; and in the second, an acetate of manganese sesquioxide.

Action of Selenyl Chloride on Mannite.—C. Chabrié and A. Bouchonnet.—A previous research treats of the action of selenyl chloride on erythrite, and now the authors extend their investigation to its action on mannite. The reaction apparently takes place according to the following equation:—



The formation of hydrochloric acid, and the temperature of the reaction, explains the dehydration, and the existence of the group SeO is shown by the fact that all the selenium can be precipitated by sulphurous acid when hot in an aqueous solution of the product.

Synthesis of Anisic Acid and Paraethoxybenzoic Acid.—F. Bodroux.—The monobromated derivatives of the phenolic oxides react with magnesium in presence of anhydrous ether. By this means organo-metallic compounds are formed which possess all the properties of chlorides, bromides, and iodides of alcoyl-magnesium. Aldehydes, acetones, ether salts, iodine, and bromine act on these salts with violence; water destroys them, and primitive phenolic oxides are formed. Finally, carbonic anhydride is absorbed, with formation of double salts of magnesium, which decompose acids whilst liberating the ether oxides of phenol acids. An application of this latter reaction to the parabromated derivatives of anisol and phenetol the author uses as a means of synthesising anisic and paraethoxybenzoic acids.

Molecular Decomposition in the Pyrane Series.—R. Fosse.—Under the influence of bromine, naphthylol-dinaphthopyrane, $OH-C_{10}H_6-CH<^{C_{10}H_6}_{C_{10}H_6}>O$, breaks up its trinaphthylmethanic molecule into two bromated molecules, $OH-C_{10}H_6-Br+CH<^{C_{10}H_6}_{C_{10}H_6}>O-Br$.

Migration of the Methyl Group under the influence of Hydriodic Acid.—E. E. Blaise.—Under the influence of hydriodic acid, one of the methyl groups in dimethol glutaconic acid migrates from position 2 to position 4.

A New Orthocyclohexanediol and its Derivatives.—Léon Brunel.—In a preceding research the author describes the preparation of a hexahydrobenzenic glycol from monohydriodic ether. This substance is orthocyclohexanediol, $OH-C_6H_{10}-I$, and the ether oxides, $CH_3O-C_6H_{10}-I$ and $C_2H_5O-C_6H_{10}-I$, of this alcohol. He now examines the products obtained by saponification of these products.

Two New Glucotannoids.—Eugene Gibson.—During an investigation on the tannoids obtained from China rhubarb, the author isolates two new glucotannoids, which he prepares in a pure crystalline state. These he calls glucogalline and tetrarine.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. The following were elected Members:—Rev. Charles H. Bowden, Mr. W. Chattaway, Mr. C. Clark, Mr. H. R. Goring, Mr. J. B. Hilditch, Mr, C. E. Kayler, Mrs. Kayler, Mr. J. R. Macdonald, Mr. H. F. Morley, Miss H. Nunes, Lady Russell Reynolds, Mr. J. Rheinberg, Mr. T. K. Rose, Mr. H. H. Shepherd, Mr. J. K. Spence, Mr. F. T. Trooton, Mrs. Vlasto, Mr. J. A. Voelcker, Mr. W. Weddell, Mr. J. W. Western, and Miss E. Willmott. The special thanks of the Members were returned to the Worshipful Company of Clothworkers for a donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures.

A Combination of Acetic Acid with Nitric Acid.—Ainé Pictet and P. Genequand.—When we add nitric acid of 1·4 density to about an equal volume of acetic anhydride, a lively reaction is produced accompanied with a sufficient evolution of heat to cause the liquid to boil. If this mixture is submitted to fractional distillation, we obtain a principal fraction which passes over at 127·7° under 730 m.m. pressure. The analysis of this fraction gives the formula $C_4H_9NO_7$ or $2C_2H_4O_2+HNO_3$. The question arose, is this substance a simple mixture or a definite compound? The determination of the molecular weight showed that $C_4H_9NO_7$ is the true formula, and that therefore we have to do with a compound. The constitution of this body is probably expressed by the following formula: $CH_3-CO-O-N(OH)-O-CO-CH_3$, and we should look upon it as a mixed anhydride of acetic acid and orthonitric acid, $N(OH)_5$; *diacetylorthonitric acid* is a colourless liquid, fuming in the air, boiling at 127·7° under 730 m.m., and at 45° under 17 m.m. Its density is 1·189 at 23°, and its refractive index $n_D = 1{\cdot}38432$ at the same temperature. Cryoscopic examination shows that diacetylnitric acid, when mixed with water, undergoes complete dissociation, and this instability makes it very improbable that salts are formed; in fact, up to the present we have obtained absolutely negative results. This acid is also dissociated by heat, and although it will distil without change, a very slight increase of temperature above its boiling-point is sufficient to decompose it. A similar product was obtained by treating propionic acid in the same manner, but the other acids in the series, such as formic, butyric, and isovalerianic acids, gave only negative results.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 16—17.

The Oxidation of Aniline.—E. Bornstein.—Aniline, in the form of a salt in dilute, neutral, aqueous solution, is oxidised in the cold by PbO_2 or MnO_2; there is an intermediate formation of an aminoquinone, which condenses with the excess of aniline, giving aminodiphenylquinonediimide, $NH_2C_6H_3(NC_6H_5)_2$; by operating in more concentrated solution azophenine is formed; the author gives 246° as the fusing-point of this latter body. Aminodiphenylquinonediimide crystallises from an acetone-alcoholic solution in thin prisms of a bluish-red colour, collected together in stars, fusible at 167°; it is soluble in benzene, acetic ether, CS_2, $CHCl_3$, acetone, and ether, and slightly soluble in alcohol; this compound dissolves in sulphuric acid, giving a red solution, which becomes bluish-violet on heating; when cooled and diluted with water we obtain a blue solution with red fluorescence (reaction of fluoridine). The reduction of aminodiphenylquinonediimide by sulphide of ammonium gives a compound fusible at 83°, giving an acetylised derivative fusible at 170—171°. By the action of aniline and its hydrochlorate with the addition of $ZnCl_2$, aminodiphenylquinonediimide is transformed into azophenine.—*Berichte*, vol. xxxiv., p. 1268.

Action of Chlorides and Anhydrides of the Acids of the Fatty Series on Polymerised Methanal.—Marcel Descudé.—If to one molecule of polyoxymethylene we add one molecule of chloride of acetyl, then a pinch of melted powdered chloride of zinc, an extremely violent reaction is soon manifested, while the polyoxymethylene disappears in a few instants. A colourless, limpid liquid is obtained which does not contain a trace of chloride of acetyl; it consists principally of chloroacetate of methylene, but it contains also bichlorised methylic ether and diacetate of methylene. If we heat a mixture, molecule for molecule, of pure acetic anhydride and polyoxymethylene to about 130°, in the presence of chloride of zinc, we observe that in a few moments the polyoxymethylene has completely disappeared as well as the chloride of zinc. After distilling *in vacuo* we recover a quantity of liquid equal to the weight of the mixture within 2 or 3 per cent. It is formed principally of diacetate of methylene, and is identical with the product resulting from the action of iodide of methylene on acetate of potassium; it is fairly soluble in water, which only decomposes it slowly; it boils at 170°, and its density at 20° is 1·136°. But this is not the only body formed during the reaction. After the distillation is complete on the water-bath an important residue remains; if we now continue the operation on an oil-bath at about 130° the thermometer rises rapidly, and remains steady at 102° at 14 m.m. pressure, although the oil-bath may be heated to more than 180° at the end. By this means we obtain a colourless liquid which, when re-distilled at the ordinary pressure, passes over almost entirely between 204° and 207°. Analysis and cryoscopy give it the formula $C_6H_{10}O_5$; its constitution is probably as follows:—

$$CH_3-COO-CH_2-O-CH_2-COO-CH_3$$

this new body is called diacetate of oxide of methylene.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 16—17.

Merck's Digest. No. 12. Lecithin.—Lecithin is an important constituent of animal and vegetable tissues occurring more especially in the nerves, the brain, the yolk of eggs, also in blood, and in the chlorophyl of plants. Generally, it is associated with the cell nucleus, and especially in young cells lecithin exists in the form of an albumenoid compound. Lecithin can be prepared from the germs of the oat or from yolk of egg, but at present is prepared for medicinal purposes almost exclusively from the latter material, under the name of ovolecithin. Chemically, lecithin is to be regarded as a distearic-glycer-phosphoric cholin ether, its composition being represented by the formula—

$$C_3H_5\begin{cases}O.CO.C_{17}H_{35}\\O.CO\,C_{17}H_{35}\\O.PO(OH)OC_2H_4N(CH_3)_3OH.\end{cases}$$

Ovolecithin is a yellowish waxy mass, soluble in hot alcohol, also in chloroform, benzene, or fat oils. In water or physiological salt solution it swells up, forming a jelly. It is recommended in cases of diseases arising from disturbances of nutrition, and for diseases of the brain and nervous system. The remarkably rapid increase of red blood corpuscles, observed as a result of the administration of lecithin, indicates that it is a valuable means of effecting blood formation. M. Serono observed in cases of chlorosis and anæmia that the increase of red corpuscles was as much as from 800,000 to 1,500,000 per c.c.; its powerful tonic action is also exercised in the most beneficial manner.

Transformation of Tartaric Acid into Oxalacetic Acid by the Elimination of Water at a Low Temperature.—A. Wohl and C. Œsterlin.—The authors have succeeded in transforming tartaric into oxalic acid in the following manner:—Diacetyltartaric acid is first prepared by Thiele's method of acetylation (acetic anhydride and sulphuric acid); it is then treated with pyridine cooled down to $-5°$; a pyridic compound is formed which the authors regard as the pyridine salt of oxymalic anhydride, which, under the action of dilute sulphuric acid, gives oxalacetic acid. This oxalacetic acid fuses at 146°, that prepared by Fenton, by applying his method of oxidation to malic acid (H_2O_2 and a salt of iron), fuses at 176°; the two bodies are transformed easily one into the other. If we treat the pyridic compound in question with aniline at the ordinary temperature, there is a violent disengagement of carbonic acid, and pyruvic anilide is collected; this has been identified with that obtained by Nef, by means of its fusion-point, its hydrazone, and by the polymer which results from the action of ammonia.—*Berichte*, vol. xxxiv., p. 1139.

MEETINGS FOR THE WEEK.

MONDAY, 9th.—Society of Arts, 8. (Cantor Lectures). "Hertzian Wave Telegraphy in Theory and Practice," by Prof. J. A. Fleming, M.A., D.Sc., F.R.S.

TUESDAY, 10th.—Royal Institution, 5. "Recent Advances in Photographic Science," by Sir William Abney, K.C.B., D.C.L., F.R.S.

WEDNESDAY, 11th.—Society of Arts, 8. "Existing Laws, By-Laws, and Regulations Relating to Protection from Fire, with Criticisms and Suggestions" (Fothergill Prize Essay), by T. Brice Phillips.

THURSDAY, 12th.—Royal Institution, 5. "Insect Contrivances," by Prof. L. C. Miall, F.R.S.

—— Society of Arts, 4.30. "The Currency Policy of India," by J. Barr Robertson.

FRIDAY, 13th.—Royal Institution, 9. "Character Reading from External Signs," by Prof. Karl Pearson, F.R.S.

—— Physical, 5. "On the Interpretation of Milne Seismograms," by Dr. Farr. "A Potentiometer for Thermo-couple Measurements" and "A Resistance Comparator," by Dr. R. A. Lehfeldt. "A Direct-reading Potentiometer for Thermo-electric Work," by Dr. J. A. Harker. "On the Measurement of Small Resistances," by A. Campbell.

SATURDAY, 14th.—Royal Institution, 3. "Light—its Origin and Nature," by Lord Rayleigh, F.R.S., &c.

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Re Pirie *v.* The Electro-Chemical Co. (1900), Ltd., 1901, E. 85.—By order of Mr. Justice Farwell.—Mr. F. J. Terry Horsey, of the firm of—

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THE CHEMICAL NEWS.

VOL. LXXXVII., No. 2259.

NOTE ON THE VOLUMETRIC ESTIMATION OF ZINC.

By J. E. CLENNELL.

A SIMPLE and accurate method for the estimation of zinc is much needed. Two principles are in general use, viz.,—

(*a*) The sulphide method.
(*b*) The ferrocyanide method.

Both require an external indicator. In the case of the sulphide method, lead salts, ferric hydrate, and sodium nitroprusside are commonly employed, but the exact finishing point is very difficult to determine. The end-point of the ferrocyanide method with uranium acetate is somewhat sharper, but cannot be regarded as altogether satisfactory.

In the method here described, the zinc is precipitated by means of a solution of sodium sulphide of known strength, added in slight excess, the excess of sulphide being then determined by making use of the reaction—

$$Na_2S+2KAgCy_2=Ag_2S+2NaCy+2KCy.$$

The solutions required are—

Sodium Sulphide.—A convenient strength being about 0·2 per cent Na_2S.

Silver Double Cyanide.—Prepared by adding silver nitrate to a solution of potassium cyanide (say, 2 or 3 per cent KCy) till a slight permanent precipitate of AgCy is produced, allowing to stand, and filtering.

Silver Nitrate.—Any dilute solution of known strength. A convenient standard is one containing 5·215 grms. $AgNO_3$ per litre, 1 c.c. being equivalent to 0·001 grm. zinc.

Potassium Iodide.—1 per cent solution.

It is perhaps advisable also to have a standard zinc solution prepared from pure metallic zinc or re-crystallised zinc sulphate, and containing (say) 0·5 per cent to 1 per cent Zn.

Method.

The zinc in ores or similar substances is brought into solution in the ordinary way, and the liquid made strongly alkaline with caustic soda or ammonia, boiled, diluted, and filtered if necessary. In cyanide solutions, the sulphide may in general be applied direct; in some cases, however, it may be necessary to remove the cyanogen by a preliminary operation.

The liquid to be tested is mixed with a measured volume of sodium sulphide, slightly in excess of that required to precipitate the whole of the zinc. The liquid is well shaken in a stoppered flask; a little lime may be added to promote settlement. The whole, or an aliquot part, is then filtered, and an excess of the double silver cyanide added. The precipitate of Ag_2S generally settles rapidly, and is easily filtered and washed (occasionally it may be necessary to add a little more lime). About 5 c.c. of the 1 per cent KI solution are added to the filtrate, and the liquid titrated with $AgNO_3$ till a slight yellowish turbidity remains permanent.

1 grm. KCy = 0·3 grm. Na_2S = 0·25 grm. Zn.

Results.

The accompanying table illustrates the results of titrations made by this method with solutions containing known quantities of zinc.

In the tests (5, 6, 7) made with zinc double cyanide, a separate portion of the original liquid was tested in the ordinary way for "total cyanide," *i.e.*, by titration with silver nitrate, using alkaline iodide indicator, and the cyanide so found deducted from the amount shown by titration after adding sodium sulphide and the double silver salt. In test No. 4, however, the cyanide was precipitated before making the estimation of zinc, by adding excess of $AgNO_3$, and then a few drops of HCl to remove excess of $AgNO_3$, boiling, and filtering; making strongly alkaline with NaOH before adding Na_2S.

In presence of ferrocyanide and thiocyanate, it appears to be necessary to make the solution strongly alkaline to ensure complete precipitation of the zinc sulphide.

Estimation of Alkaline Sulphides.

It is obvious that the same principle may be applied for the estimation of alkaline sulphides. The results with solutions containing varying amounts of sulphide are very closely proportional to the amount of sulphide used. When the liquid to be tested also contains cyanides, a separate portion of the original liquid must be titrated with $AgNO_3$ and iodide indicator after treatment with lead salts to remove sulphide, and the necessary correction applied.

No. of test.	Weight of $ZnSO_4.7H_2O$ taken.	Weight of K_2ZnCy_4 taken.	Weight of $K_4FeCy_6.3H_2O$ added.	Weight of KCNS added.	Weight of Na_2S added.	Weight of Zn found.	Weight of Zn present (by theory).
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
1.	0·2215	—	—	—	0·0855	0·0495	0·0500
2.	0·4430	—	—	—	0·1334	0·1004	0·1000
3.	0·4450	—	—	—	0·1710	0·1017	0·1004
4.	—	0·10	—	—	0·0427	0·0264	0·0263
5.	—	0·10	—	—	0·0654	0·0258	0·0263
6.	—	0·10	0·05	—	0·0654	0·0265	0·0263
7.	—	0·10	—	0·05	0·0654	0·0274	0·0263

A Synthesis of Naphthoïc Acid and of Naphthalene.—E. Erlenmeyer and J. Kunlin.—This synthesis is based on the decomposition of cinnamylidene-hippuric acid, obtained by condensing cinnamic aldehyde with hippuric acid. By heating this acid with hydrochloric acid in sealed tubes at 110°—120° for eighteen hours, we observe a very strong odour of naphthalene on opening the tubes. In fact, the authors have isolated naphthalene from the product of the reaction; it fuses at 79°—80°, and, further, they obtained a mixture consisting of cinnamylidene-hippuric acid unchanged, benzoïc acid, and α-naphthoïc acid. Their intention was to transform first the cinnamylidene-hippuric acid into α-ketonic acid by reacting with alkalis on the said acid, but this process was accompanied by secondary reactions, which did not allow them to isolate the ketonic acid; by the action of hydrochloric acid, the α-ketonic acid, which ought to have been formed, is immediately transformed into α-naphthoïc acid and naphthalene, as has just been shown. The authors propose to examine some analogous reactions with the object of obtaining other derivatives of naphthalene.—*Berichte*, vol. xxxv., p. 384.

ON THE COMPLEX SALTS OF PLATINUM. PLATO-OXALONITRITES AND PLATO-OXALONITROUS ACID.

By M. VÈZES.

PLATO OXALONITRITE of barium, $Pt(C_2O_4)(NO_2)_2Ba,5H_2O$, of which the preparation and the principal properties have been described in a previous paper (*Bull. Soc. Chim.*, 1901, Series 3, vol. xxv., p. 157), will serve for the preparation of other salts, derived, as it is, from a plato-oxalonitrous acid having the formula $Pt(C_2O_4)(NO_2)_2H_2$.

I. *The Sodium Salt.*—Twelve grms. of plato-oxalonitrite of barium are dissolved rapidly in about 200 c.c. of boiling water, and treated with 20 c.c. of a solution of sulphate of soda containing 1 molecule of this salt per litre. An abundant white precipitate is formed, which collects easily at the bottom of the vessel. After cooling and filtering, the filtrate is evaporated rapidly. On the other hand, the precipitated sulphate of barium is washed, collected, and weighed; its weight is found to be 4·69 grms., and the theoretical weight calculated from the amount of material used is 4·67 grms.

When the filtrate is reduced by evaporation to about 10 c.c., it is allowed to cool, and the plato-oxalonitrite of sodium is deposited in the form of tabular crystals of a deep yellow colour, and corresponding to the formula $Pt(C_2O_4)(NO_2)_2Na_2+H_2O$.

The first deposit weighs 6 grms., the theoretical amount of the salt that should be obtained being 8·8 grms. The slow evaporation of the mother-liquor enables us to obtain the remaining 2·8 grms.

The salt thus obtained, of which M. Dufet has kindly made the crystallographic examination, occurs in the form of triclinic crystals, having facets $p(001)$, $o\frac{1}{3}(301)$, $a^1(10\bar{1})$, $i^1(011)$, and $e\frac{1}{3}(03\bar{1})$. Some of them are more simple, and have only the facets p, i^1, and a^1, this latter being striated parallel to the edge $p\,a^1$.

They have a perfect cleavage along $o\frac{1}{3}$.

Triclinic System.

$a : b : c = 0{\cdot}68153 : 1 : 0{\cdot}94068.$

Plane Angles.		*Dihedric Angles.*	
$\alpha\,(b\,c)$ ..	89° 48′ 40″	A $(p\,g^1)$ ..	89° 53′ 45″
$\beta\,(a\,c)$ ..	90° 41′ 45″	B $(p\,h^1)$ ..	90° 40′ 40″
$\gamma\,(a\,b)$ ..	97° 6′ 20″	C $(h^1\,g^1)$..	97° 6′ 15″

Perpendicular Angles.

	Calculated.	Measured.
$p\,o\frac{1}{3}$ (001) (301)	Base	*75° 53′
$a^1\,o\frac{1}{3}$ $(10\bar{1})$ (301)	Base	*49° 23′
$p\,a^1$ $(00\bar{1})$ $(10\bar{1})$	54° 44′	54° 45′
$p\,i^1$ (001) (011)	Base	*43° 31′
$i^1\,e\frac{1}{3}$ (011) $(03\bar{1})$	Base	*65° 57′
$p\,e\frac{1}{3}$ $(00\bar{1})$ $(03\bar{1})$	70° 32′	70° 31′
$a^1\,i^1$ $(\bar{1}01)$ (011)	69° 34′	69° 33′
$i^1\,o\frac{1}{3}$ (011) (301) ..	74° 58′	74° 53′
$a^1\,e\frac{1}{3}$ $(10\bar{1})$ $(03\bar{1})$	Base	*73° 17′
$o\frac{1}{3}\,e\frac{1}{3}$ (301) $(03\bar{1})$	91° 49′	91° 48′

When dried in the cold on filter-paper, these crystals do not change in the air.

When submitted to the progressive action of heat they lose 1 molecule of water of crystallisation; but this dehydration, which is slow at about 100°, only becomes rapid when the temperature reaches 150° or 200°.

The greyish-yellow powder obtained in this manner, when heated more strongly, decomposes very rapidly at about 270°, like plato-oxalonitrite of potassium, according to the equation $Pt(C_2O_4)(NO_2)_2Na_2 = Pt + 2NO_2Na + 2CO_2$.

Plato-oxalonitrite of sodium is very soluble in water; in fact, it dissolves in about four times its own weight of cold water and in its own weight of boiling water. Its solutions are very stable.

The analysis of this salt, made by the methods I have already described for the potassium salt, gave the following results:—0·9472 grm. of material, heated to 200°, lost 0·0401 grm. of water; the dry product, decomposed by heat at 270°, left a residue weighing 0·7241 grm. This residue, calcined with an excess of sulphuric acid, gave a mixture weighing 0·7283 grm., and composed of 0·4224 grm. of platinum, and 0·3059 grm of sulphate of sodium, containing 0·0992 grm. of sodium.

	Calculated.		Found.
		Per cent.	Per cent.
Pt	194·8	44·37	44·59
2Na	46 1	10·50	10·47
2C	24 0	5·47	—
2N	28 1	6·35	—
8O	128 0	29·21	—
H_2O	18·0	4 10	4·23
$Pt(C_2O_4)(NO_2)_2Na_2+H_2O$	439·0	10 ·00	—
$Pt+2NO_2Na$	333 0	75·85	76·45
$Pt+SO_4Na_2$	337 0	76·77	76·89

II. *The Ammonium Salt.*—A reaction similar to that which gave the preceding salt also enables us to obtain a solution of the corresponding salt of ammonium; by operating, as has been described above, with 12 grms. of plato-oxalonitrite of barium and 20 c.c. of a solution of sulphate of ammonium containing 1 molecule of the salt per litre, we obtain a deposit of sulphate of barium corresponding almost exactly to the whole of the barium and the sulphuric acid contained in the mixture (calculated, 4·67 grms. of sulphate of barium; found, 4·63 grms.). The yellow liquor, freed from the precipitate by filtration, should thus give by evaporation plato-oxalonitrite of ammonium; but whether we concentrate by heat or whether we leave it to spontaneous evaporation in a dry atmosphere in the cold, we observe that its concentration is accompanied by a disengagement of gas, which is a certain sign of decomposition. When carried out to the end, evaporation gives as a residue non-crystallisable products, of which it did not appear to be useful to continue the examination.

Plato-oxalonitrite of ammonium, of which we may remark the probable formula contains the elements of nitrite of ammonium, thus appears to be too unstable to be isolated in the crystalline form.

III. *Plato-oxalonitrous Acid.*—The same method appears to lead us to the acid from which the preceding salts are derived; we treated 7·57 grms. of plato oxalonitrite of barium, dissolved in 150 c.c. of warm water, with the equivalent amount of dilute sulphuric acid (50 c.c. of a titrated solution containing 0·2514 molecule of acid per litre).

The mixture of the warm solutions immediately gave a precipitate of sulphate of barium corresponding to the whole of the sulphuric acid and the barium contained in the solutions mixed (calculated, 2·93 grms. of sulphate of barium; found, 2·96 grms.). The filtrate obtained was limpid and of a bright yellow colour, and did not give a white precipitate with either sulphuric acid or chloride of barium; thus, it is free from barium and from sulphuric acid; but the latter of these reagents gave slowly and in the cold a deposit of yellow crystals of plato-oxalonitrite of barium. In the same way it gives a deposit of yellow crystals of plato-oxalonitrite of potassium, with a solution of a potassium salt. There is no doubt, therefore, that this yellow liquid is a solution of the plato-oxalonitrous acid, $Pt(C_2O_4)(NO_2)_2H_2$, corresponding to these salts.

But this acid is very unstable in concentrated solutions, for, if we evaporate this solution, either by the action of

heat or of a vacuum, or even slowly in the cold in dry air, it becomes red, and gives off nitrous fumes which are the evident signs of decomposition. Eventually it becomes syrupy, and takes a deep blue colour, without giving any crystalline deposit. Thus, plato-oxalonitrous acid appears to be too unstable to be obtained in any other state than that of a solution.

IV. *The Case of the Salts of Heavy Metals.*—Finally, we have endeavoured to prepare, by the same method, plato-oxalonitrites of the heavy metals; as an example, we will give the case of copper. Twelve grms. of plato-oxalonitrite of barium were dissolved in warm water and treated with 20 c.c. of a solution of sulphate of copper at 1 molecule per litre. The abundant precipitate formed by the mixture of these solutions had a bluish tint; its analysis showed that it contained, besides the whole theoretical amount of sulphate of barium which ought to be formed by the reaction (calculated, 4·67 grms.; found, 4·66 grms.), a quantity of oxalate of copper containing nearly the whole of the copper and the oxalic acid present in the mixed solutions (it gave 1·4 grms. of oxide of copper instead of 1·6 grms.). The filtrate, on evaporation, gave, besides a deposit of oxalate of copper containing the remainder of the oxalic acid and the copper used, products similar to those formed by the decomposition of plato-nitrous acid, notably a red substance, probably identical with the triplato-octonitrous acid of M. Nilson (*Berichte*, 1877, vol. x., p. 934).

Thus it appears to result from this experiment that the plato-oxalonitrites of the heavy metals are still less stable, in the presence of water, than the acid from which they are derived, and cannot be obtained in the stable condition in solution. We may add that we have already been brought to the same conclusion by another means (*Bull. Soc. Chim.*, vol. xxvii., p. 932), when examining the action of the salts of the heavy metals on solutions of plato-oxalonitrite of potassium.—*Bull. Soc. Chim.*, Series 3, vol. xxix. No. 2.

THE ESTIMATION OF DIGITALIN IN PHARMACOPŒIAL PREPARATIONS OF DIGITALIS AND DIGITALIN.*

By M. ECALLE.

Throughout this paper the term "digitalin" will apply exclusively to the crystallised digitalin of the French Codex, obtained for the first time by M. Nativelle. This digitalin is completely soluble in chloroform and identical with the German *digitoxin* of Schmiedeberg.

The product called digitalin by this latter chemist is a glucoside of digitalis of which the physiological action is very different to that of the French digitalin.

Therefore it is necessary to establish very distinctly the difference between the two products so unfortunately designated by the same name, the more especially since Kiliani (*Journ. de Pharm. et de Chim.*, 1899, Series 6, vol. ix., p. 57) has been able to produce German digitalin in the crystalline form.

Crystallised French digitalin has the following characteristics:—It is insoluble in water, easily soluble in alcohol and in chloroform, less soluble in ether, and insoluble in petroleum ether. German digitalin is insoluble in water, and soluble in alcohol, but insoluble in chloroform.

French crystallised digitalin and German digitalin, further, have particular reactions which enable one to be distinguished from the other, when they are dissolved in concentrated sulphuric acid and an oxidising solution is added, such as bromine, nitric acid, or perchloride of iron.

Kiliani was the first to devise a practical method of operating, and it is this method slightly modified by Keller, and then again by Kiliani, that we have followed.

The two following solutions are prepared as reagents:—

Solution No. 1.

Pure sulphuric acid	100 c.c.
Solution of iron-alum at 5 per cent ..	1 ,,

Solution No. 2.

Glacial acetic acid	100 c.c.
Solution of iron-alum at 5 per cent ..	1 ,,

Method of Operating.—About 4 or 5 c.c. of solution No. 1 are poured into a test-tube. At the same time we dissolve in another test-tube, or better still in a test-glass, a trace of digitalin in about half a c.c. of solution No. 2; one drop of perchloride of iron is added to this latter, and this is then allowed to run slowly down the side of the tube containing solution No. 1, and remain a few minutes in contact.

With French digitalin, at the point of contact between the two layers of liquid, a dark coloured zone is formed, and above this, and consequently in the acetic acid, an absolutely characteristic blue-green ring.

With German digitalin, this blue-green colouration in the upper portion is not produced, but the lower portion (ferric sulphuric acid) becomes reddish-violet in colour.

The simultaneous appearance of both these reactions enables us to detect a mixture of both the digitalins (Kiliani, *Journ. de Pharm. et de Chim.*, 1896, Series 6, vol. iv., p. 29).

According to Keller (*Journ. de Pharm et de Chim.*, 1897, vol. vi., p. 167), crystallised French digitalin being much the most active of all the glucosides found in, and isolated from, digitalis, we may conclude that the value of a digitalis, or of its preparations, should be proportional to the amount of crystallised digitalin it contains. To effect this, estimation would be therefore a means of fixing its value.

It is this that we have endeavoured to do. The method we adopted was that of Keller (*loc. cit.*, p. 168). After several trials, however, we found it advisable to make some modifications, which give, in our opinion, much greater accuracy to the results.

The process we have finally decided on was tested on a solution of digitalin mixed with an inactive dissolved extract (extract of "dog's tooth").

0·236 grm. of crystallised digitalin was dissolved in 5 c.c. of alcohol at 90°, and then mixed with a solution of 2 grms. of extract of dog's tooth in a sufficient quantity of distilled water, the total volume being made up to about 150 c.c. This solution is treated with 25 c.c. of 1 in 10 neutral acetate of lead, and the volume then made up to exactly 200 c.c.

After well stirring and filtering, 100 c.c. of the filtrate were taken. These 100 c.c. were treated with 10 c.c. of a solution of sulphate of soda at 50 per cent to remove the excess of lead. After standing for forty-eight hours, 90 c.c. of the clear liquid were removed by decantation.

It is on these 90 c.c., which represent $\frac{9}{20}$ths of the total volume of liquid, that the actual estimation of the digitalin is to be made. However, this volume of 90 c.c. is not fixed arbitrarily; we simply decanted as much of the clear liquid as possible, and used this solution after having measured its volume exactly.

To the decanted liquid we added 2 c.c. of 10 per cent ammonia and 30 c.c. of chloroform. The whole is then poured into a bulb vessel of about 250 c.c., fitted with a tap, and shaken moderately (about 20 or 30 shakes), then left to settle. The decanted chloroformic solution is filtered, preferably through a filter-paper moistened with chloroform.

The operation is repeated five times with an equal volume of chloroform. Sometimes it is necessary, in order to exhaust the liquors completely, to shake more vigorously in some of these operations. An emulsion may commence to be formed, in which case the whole must be

* A Paper read before the Société de Pharmacie, Feb. 4th, 1903.

left to stand for forty-eight hours. All the chloroformic liquors, united in one beaker, are evaporated on a water-bath, and dried by means of a current of hot air.

When the evaporation is completely finished, the residue is re-dissolved in about 3 c.c. of chloroform, and the chloroformic solution placed in another Bohemian glass beaker previously tared, and of about 100 c.c. capacity.

To this solution we add 10 c.c. of sulphuric ether of 0·720 density, and 70 c.c. of petroleum ether.

The mixture is shaken carefully, and left to settle for forty-eight hours, after taking care to cover the beaker with a clock glass, so as to prevent a too great evaporation of the solution.

The clear liquid is then decanted as far as possible, and the remainder evaporated, first on a water-bath, and then when very little liquid is left, about 1 c.c., it is dried by means of a current of hot air.

The beaker is then placed in a desiccator, and weighed after cooling.

The amount of digitalin obtained was 0·0098 grm., or, for the total quantity of solution, $\frac{0{\cdot}0098 \times 110}{90} \times 2 = 0{\cdot}0239$ grm. instead of the 0·0236 grm. originally taken.

By this method we have estimated the digitalin in several preparations of digitalis.

Results.

The following are some of the results we have obtained:—

1. *In a Commercial Tincture of Digitalis made according to the Formula in the Codex.*—The estimation was made on 100 grms. of the tincture, which were evaporated on the water-bath down to 10 c.c. These 10 c.c. were taken up with 100 c.c. of distilled water, and the estimation proceeded with as above.

We found 0·0398 grm. of digitalin in the 100 c.c. of tincture of digitalis; that is, 0·398 per 1000.

Under these conditions digitalin occurs, as Keller observed, in the form of a partially crystallised varnish. It is not absolutely pure when operating with a tincture, an extract, or with leaves, but contains slight traces of German digitalin. The estimation completed, a trace of the 39 8 m grms. of digitalin obtained gave the characteristic reaction of identity.

The same verification was done for each of the estimations made in the course of this research.

2. *In an Etherial Tincture of Commercial Digitalis made according to the Formula in the Codex.*—100 grms. of the etherial tincture of digitalis were evaporated with the necessary precautions, the residue taken up with distilled water, and the evaporation continued as above. Result:—0·02337 grm. per 100 grms. of the tincture; that is, 0·2337 grm. per 1000.—*Journ. de Pharm. et de Chim.*, Series 7, vol. xvii., No. 5.

Some Metallic Fluorides in the Dissolved State.—A. Jœger.—Mercuric fluoride in solution is to a great extent hydrolysed (80 per cent), and the examination of the hydrolysis points to the formula H_2F_2 for hydrofluoric acid. With cupric fluoride the hydrolysis is much less considerable. The solubility of fluoride of cadmium in water is 0·3 molecule, its solubility in hydrofluoric acid is much greater; apparently there is a formation of a hydrofluorate of the fluoride. Fluoride of lead is distinguished from the other halogen salts of lead by its extremely slight solubility in water, 5·5 milli-molecules per litre. The hydrate, $Pb(OH)_2$, decomposes the alkaline halogen salts until a certain equilibrium is established owing to the formation of free alkali. The same phenomenon can be observed by substituting the halogen salts of lead for the alkaline salts; under these conditions, either a basic or a complex salt is formed.—*Zeit. Anorg. Chemie*, vol. xvii., p. 22.

ON THE ACTION OF CARBONIC OXIDE ON THE MANGANO-, COBALTI-, CHROMO-, AND PLATINO-CYANIDES OF POTASSIUM.

By J. A. MULLER.

THE decided action of carbonic oxide on ferro- and ferricyanide of potassium, with the formation of carbonylferrocyanide, induced me to try if the other complex cyanides were susceptible of reacting on this gas with the formation of the corresponding carbonylcyanides.

With this object I have made two series of experiments; in the first series, I heated an aqueous solution of the cyanide under examination in an atmosphere of carbonic oxide in sealed tubes for fifty hours at about 130°; in the second series, I heated the same solutions for thirty-six days at about 70°.

We will examine first the results obtained with manganocyanide of potassium, and then those given by the three other cyanides.

Manganocyanide of Potassium.—This crystallised salt was used in the form of good though small crystals of a violet-blue colour, and was obtained by re-crystallising in a solution of cyanide of potassium, the blue crystalline precipitate prepared by reacting with small pieces of cyanide of potassium on a solution of manganous acetate.

In a preliminary experiment 1·25 grms. of the manganocyanide, dissolved in 10 c.c. of a solution of cyanide of potassium, was heated to 130°, in the presence of 0·110 grm. of carbonic oxide. After heating, an absorption of 0 035 grm. of this gas was observed; the liquid in the tube had a very pale yellow colour; it was ammoniacal, but still contained cyanide of potassium. As this liquid was easily oxidisable in the air, it was collected in a flask full of nitrogen. With an excess of sulphate of zinc it gave a pure white gelatinous precipitate, whereas a solution of manganocyanide in dissolved cyanide of potassium gives a violet-blue precipitate with this sulphate.

In a second experiment, 1·157 grms. of manganocyanide treated with 5 c.c. of water (which gave rise to the formation of a green precipitate of mangano-potassic manganocyanide, $MnK_2Mn(CN)_6$), was heated to 130° in the presence of 0·090 grm. of carbonic oxide, of which 0·011 grm. was absorbed. The characteristics of the solution contained in the tube after heating, were practically the same as those in the first experiment. The same is the case with the solutions obtained in the experiments made at 70°:—

	Manganocyanide dissolved in 5 c.c. of concentrated solution of KCN.	Manganocyanide treated with 5 c.c. of water.
	Grm.	Grm.
Weight of manganocyanide of potassium used	1·208	1·157
Weight of CO used	0·099	0·099
Weight of CO absorbed ..	0·025	0·009

The total transformation of the manganocyanide into carbonyl-manganocyanide analogous to the carbonylferrocyanide, would require, for 1·25 grms. of dry manganocyanide, an absorption of 0·095 grm. of carbonic oxide. Now, in all the experiments made, the amount of carbonic oxide absorbed has been always very far from this weight. This absorption of carbonic oxide, however, was never negligible, but it may be attributed—for the most part at any rate—to the alkalinity of the solution in which the reaction took place, an alkalinity which was considerable, especially in solutions containing an excess of free cyanide of potassium. As for the absence of manganocyanide in the different liquids from the tubes, after heating, it must be caused by an almost complete hydrolysis of the molecule of manganocyanide, a molecule which is, as is known, much less stable than that of ferrocyanide of potaasium.

Cobalti-, Chromo-, and Platinocyanides of Potassium.—The first of these salts was obtained by dissolving

	$K_2Co(CN)_6$, 2·5 per cent solution.	$K_3Cr(CN)_6$, 3 per cent solution.	$K_2Pt(CN)_4$, 3·5 per cent solution.
$FeCl_2$	White precipitate, slightly yellowish.	Brick-red precipitate.	Voluminous white precipitate.
$FeCl_3$	Nothing at first; then pale yellow cloudy precipitate.	Nothing at first; then brown precipitate.	Nothing first; then yellowish white precipitate.
$Co(NO_3)_2$	Rose precipitate.	Flocculent rose precipitate.	Pale lilac precipitate.
$NiCl_2$	Pale green gelatinous precipitate.	Blue-green gelatinous precipitate.	Very pale green precipitate.
$MnSO_4$	White precipitate.	Yellowish white crystalline precipitate.	Nothing.
$ZnSO_4$	Milky white precipitate.	Yellowish white crystalline precipitate.	White crystalline precipitate.
$Cu(C_2H_4O_2)_2$ ..	Turquoise blue precipitate.	Pale blue precipitate.	Pale greenish blue voluminous precipitate.
$AgNO_3$	Gelatinous white precipitate.	Pale yellow gelatinous precipitate.	Gelatinous white precipitate.
$Hg_2(NO_3)_2$ . ..	White precipitate.	White precipitate, turning grey.	Ultramarine precipitate.
$HgCl_2$..	Nothing; then white precipitate.	Yellow colour.	Crystalline white precipitate.
$Pb(C_2H_4O_2)_2$ ..	Nothing.	Nothing.	Nothing.
$UO_2(NO_3)_2$ . ..	Nothing.	Nothing.	Nothing.

cobaltous cyanide in a solution of cyanide of potassium, filtering, oxidising in the air, saturating with carbonic oxide, filtering a second time, acidulating with acetic acid, precipitating with alcohol, re-dissolving the washed precipitate in water, and precipitating a second time with alcohol, and finally draining and drying at 105°.

I obtained chromocyanide of potassium in magnificent amber-yellow crystals by following Odin Christensen's method (*Journ. f. Prakt. Ch.*, 1885, vol. xxxi., p. 163).

As for the platinocyanide, I bought it at M. Poulenc's. Its analysis gave H_2O, 12·43 per cent of the crystalline salt (theory for $K_2Pt(CN)_4,3H_2O$, 12·53 per cent); in the dry salt I found Pt = 51·77 and K = 20·58 (theory requires 51·63 and 20·75).

When dissolved in water the platinocyanide does not undergo any modification on heating, either to 70° or to 130°, in an atmosphere of carbonic oxide. Under the same conditions, the solution of cobalticyanide deposits a slight rose-coloured precipitate, apparently formed of cobaltous cobalticyanide still containing potassium; the weight of this precipitate was 0·023 grm. in the experiment at 130°, and 0·008 grm. in that at 70°. Finally, chromocyanide in solution is almost entirely decomposed at 130°; an abundant green precipitate is formed, consisting principally of oxide of chromium, while the solution contains only a trace of chromocyanide; during the reaction formates are produced as well as ammonia, but no carbonates or oxalates. At a temperature of 70° the decomposition of the chromocyanide is much less (0·005 grm. Cr_2O_3 for 0·999 grm. of $K_3Cr(CN)_6$).

Below I give the quantities of the different compounds used in the experiments, and the weights—always very small—of the oxide of carbon absorbed in the experiments at 130° for fifty hours, and at 70° for thirty-six days :—

	$K_3Co(CN)_6$.		$K_3Cr(CN)_6$.		$K_2Pt(CN)_4,3H_2O$.	
	At 130°. Grm.	At 70°. Grm.	At 130°. Grm.	At 70°. Grm.	At 130°. Grm.	At 70°. Grm.
5 c.c. of aqueous solution containing.. ..	1·011	1·015	0·999	0·999	1·204	1·186
CO used	0·074	0·091	0·085	0·088	0·086	0·088
CO absorbed ..	0·002	0·002	—	0·002	0·004	0·003

After heating, either at 70° or at 130°, the solutions of cobalti- and platinocyanide are neutral, and—as a result of comparative trials made—have the same action with reagents as before heating, except that the tints of the coloured precipitates obtained with the solutions of cobalticyanide of potassium when heated are very slightly paler than those obtained with unheated solutions.*

As for the dissolved chromocyanide, it is completely decomposed—as has been said already—at 130°; after heating to 70°, the solution contained in the tube is yellow, with an odour slightly ammoniacal but distinctly hydrocyanic; further, it has the characteristics of chromocyanide of potassium, except that the precipitate formed by acetate of copper is greenish blue instead of being bright blue.

In the accompanying table I have summarised the characteristics of the three latter salts of which I have just spoken, characteristics which have enabled me to indentify them before and after heating in an atmosphere of carbonic oxide.

Remarks.—All the precipitates formed by cobalticyanide of potassium are insoluble in sulphuric acid at 15 per cent even when boiled.

The precipitate formed by the platinocyanide with $FeCl_2$ is soluble hot, and that obtained with $FeCl_3$ is soluble in the cold in sulphuric acid at 15 per cent. The other precipitates are insoluble; that formed with $Hg_2(NO_3)_2$ is decomposed by sulphuric acid.

With the exception of the precipitates formed with $AgNO_3$ and $Hg_2(NO_3)_2$, all the precipitates obtained with the chromocyanide are soluble on boiling in sulphuric acid at 15 per cent, with the evolution of hydrocyanic acid.

To sum up, the preceding experiments show that:—(1) The cobalti-, chromo-, and platinocyanides of potassium do not appear to be able to form carbonylcyanides analogous to the carbonyl ferrocyanide of potassium, and that the existence of a carbonyl manganocyanide of potassium is doubtful; (2) that the mangano- and chromocyanides of potassium are much less stable in the presence

* Before heating, these solutions are of a pale yellow colour; after heating, especially at 130°, they are almost colourless.

of water than the corresponding ferro- and ferricyanides. In the case of the chromocyanides obtained by double decomposition, it was specially noticed that the precipitates formed are soluble, for the most part, in dilute sulphuric acid, with the evolution of hydrocyanic acid, the same as the simple double cyanides.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 1.

THE EFFICIENCY OF ELECTRIC FURNACES.*

By JOSEPH W. RICHARDS.

An electric furnace is a furnace for accomplishing a physical or chemical change in materials by means of the agency of heat, said heat being supplied by the transformation of electric energy. The change or effect on the materials treated being due to the heating, the output of the furnace or the capacity, as measured by amount of material treated and amount of product obtained, will be more or less proportional to the amount of heat energy developed in the furnace. I say "*more* or *less* proportional" because, although the amount of heat necessary to produce the change in a given amount of material may be a perfectly definite quantity, yet the proportion of the heat developed in the furnace which is actually absorbed or applied in producing this change is a variable one, being always less than 100 per cent, and frequently very much less. The proportion of the heat energy of the electric current thus applied to producing the useful physical, or physical and chemical, change in the charge, is what I term the *efficiency* of the furnace.

The usefully applied heat will include one or both of two factors. The first factor is, the amount of heat necessary to heat the charge up to the temperature of the furnace. This is a physical change, and is found by taking into consideration the items of the charge, their specific heats in the solid state, also their specific heats in the liquid state, and their latent heats of fusion, if they are melted, and the temperature to which they are heated. We thus obtain the quantity of heat necessary to bring them, and thence the whole charge, up to the working temperature of the furnace. My friends who are fond of mathematical expressions can easily put this proposition into the shape of a simple formula, but the matter will be easily understood as expressed above. In some electric furnace operations this is the only result aimed at, and the ratio of this amount of heat to that generated by the conversion of the electric current into heat energy, will be the useful effect or *efficiency* of the operation. The second factor, which appears in many, and in fact in the majority, of cases, is the heat absorbed in chemical reactions between the constituents of the charge when they are heated to the reacting point, which is the temperature of the furnace. This is a thermochemical question. The physical state which conditions a chemical reaction is usually *fluidity*, coupled with opportunity for gaseous products of the reaction to escape from the sphere of reaction as soon as they are formed. This is a condition analogous to the insolubility of a possible product in a solution, which factor usually conditions a chemical reaction in solution by removing from the sphere of reaction the least trace of the new product as soon as formed, and therefore causing its formation to continue if there is the slightest predisposing tendency to its production. The reactions thus brought about in the charge in electric furnace operations are usually heat-absorbing reactions, and the heat thus absorbed must be supplied by the furnace; that is, taken from the energy of the current. This amount must then be added to the heat required to bring the charge up to its reacting temperature, and the sum constitutes the usefully applied heat, and its ratio to the whole heat energy of the current is what I would term the *efficiency* of the furnace.

The degree of efficiency thus attainable depends on many factors, a partial enumeration of which is: Size of the furnace, temperature of the reaction, protection from radiation, management of the terminals, feeding and tapping, general management. Of these, by far the most important, in commercial practice, is the size of the furnace. Large bodies cool much more slowly than small ones, and this is because their radiating surface, by which they lose heat, is *proportionately* so much smaller. A suspended cube of any material, one metre on its edge, has one cubic metre volume to six square metres radiating surface; if one decimetre on its edge, it has one litre volume to six square decimetres radiating surface. That is, for one-thousandth the volume it has one-hundredth the radiating surface. Expressing it the other way, the larger cube has only one-tenth the radiating surface of the smaller one *per unit of volume or contents*. It follows that if the two cubes are heated to the same temperature, the larger one will lose only one-tenth as much heat in a given differential of time, per unit of contents, as the smaller one. If, therefore, it is wished to operate a furnace at a given fixed temperature, the loss by radiation is reduced very greatly by increasing the size of the furnace and the scale of the operation. The capacity or contents of the furnace increases approximately as the cube of the linear dimensions; the radiating surface, conditioning the loss of heat, increases as the square of the linear dimensions; therefore the proportion of radiating surface to unit of contents *decreases* approximately in proportion as the linear dimensions are increased. Make a circular furnace of twice the diameter and twice the height, its cubic capacity is increased eight times, and its radiating surface four times, and if eight times the current energy is used there will be approximately only half as much percentage loss by radiation in the larger furnace. This consideration alone would indicate the probability that if a 100 horse-power electric furnace was working at an efficiency of 50 per cent with the other 50 per cent lost by radiation and conduction, that an 800 horse-power furnace of the same design working the same process at the same temperature, should lose only 25 per cent and give an efficiency nearer to 75 per cent. Indeed, it is quite conceivable that at the limit, a change from working a furnace process from the smallest practicable scale to the largest practicable scale, might convert an operation working at 10 per cent efficiency and 90 per cent loss into an operation of 90 per cent efficiency and 10 per cent loss. Along with the increased size, where possible, comes also, in general, greater uniformity of working, regulation of temperature and control of the process, so that most of *desiderata* of commercial success lie in the direction of increasing the size of the furnaces to the furthest limit set by mechanical or physical considerations.

Dr. Borchers has classified electric furnaces into the resistance type and the arc type, the former being subdivided into those in which the material to be heated is heated by its own resistance, or by the resistance of a contiguous conductor, the latter being subdivided into those in which the charge is fed directly into the arc or is heated by radiation from the arc. For the purposes of our calculations of *efficiency*, however, we will classify the operations according to the nature of the change brought about in the charge, and therefore distinguish, first, operations in which the charge undergoes simply a physical change, and second those in which the change is both physical and chemical. The first class would include those in which the charge is simply heated without melting as well as those in which it is fused; the second would include those in which *chemical* change takes place without melting the charge, or with a fusion of the same. As types of these four classes we might mention, in their order, the graphitisation of carbon, the melting of alumina, the production of carborundum, the production of barium oxide.

* A Paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, N.Y., September 15th, 1902. From the *Transactions of the American Electrochemical Society*, ii., p. 51.

Siemens tried to introduce on a commercial scale the electrical fusion of steel by an electric arc. He has stated that the results he obtained on an experimental scale showed 50 per cent of the heat energy of the current to have been utilised. This was, however, on a small scale, using but 2 horse-power, and a greater efficiency would certainly have been attained working on a larger scale. This class of operations however, as we will see later, seem to give a higher efficiency than those in which chemical changes supervene.

Heating alone without Fusion.

As example of this we will take the conversion of anthracite coal into graphite, in the Acheson furnaces. It is true that some chemical changes probably occur during the conversion, such as the progressive formation and decomposition of carbides, but these are negligible because of their plus and minus heat quantities neutralising each other; the change from amorphous carbon to graphite is a heat-*evolving* reaction, and therefore must be reckoned as really *assisting* the current, or practically diminishing in our figuring the calculated efficiency.

The data are as follows: 1000 horse-power in twenty hours converts 12,000 pounds of anthracite into 10,000 pounds of graphite. Assumed temperature of the furnace 3300° C.; specific heat of coal to that temperature 0·5; heat of conversion 236·5 calories per pound of graphite formed.

N.B. [For convenience we will use *pound calories* (per 1° C.), as giving all figures needed for our calculations of efficiency without transposing the data.]

Heat equivalent of the current: 20,000 cal. per minute = 24,000,000 cal. per 20 hours.

Heat used in heating charge: 12,000 × 0·5 × 3300 = 19,800,000 cal. = 82·5 per cent.

Heat gained in conversion into graphite: 10,000 × 236 5 = 2,365,000 cal., or an amount equal numerically to 10 per cent of the heat supplied by the current.

Heat lost by radiation and conduction: 100 − 82·5 = 17·5 per cent of the heating power of the current.

Efficiency: The real amount of heat available was 100 + 10 = 110 per cent of the heating power of the current. Of this 82·5 per cent was utilised, giving an efficiency of 82·5 ÷ 110 = 75 per cent.

In the Acheson process of graphitising electrodes by placing them crosswise embedded in a resistant material, a considerably smaller proportion of the energy goes into the articles being graphitised because the resistance material has also to be heated to the temperature of graphitisation. In this case, the actual heat furnished to the carbons being graphitised is approximately half of the total heat absorbed by the charge, and only 38 per cent of the total heat available.

Data: 1000 horse-power graphitises 7000 pounds of electrodes embedded in 7000 pounds of granular carbon and lining.

Energy of current: 28,800,000 pound calories.

Heat in electrodes: 7000 × 0·5 × 3300 = 11,550,000 calories.

Heat of conversion: 7000 × 236·5 = 1,655,500 calories.

Total heat available: 30,455,000 calories.

Net efficiency of operation $\frac{11,550.000}{30,455,000}$ = 38 per cent. applied to useful purpose.

Heating alone with Fusion.

The Jacobs' process of fusing calcined bauxite is an illustration. The process is simple fusion by the arc in a cylindrical pot.

Energy of current: 215 horse-power for fourteen hours = 3,612,000 pound calories per run.

Heat in charge:—The heat in liquid alumina has not been determined experimentally. From a consideration of the heat in liquid slags and the temperature of the furnace, it is thought that 880 pound calories per pound of liquid alumina is a probable value. This would make the heat in 3000 pounds of charge 2,640,000 calories = 74 per cent of the total energy available.

Heating and Chemical Change, without Fusion.

The manufacture of carborundum is a good example. A mixture of carbon, silica sand, and salt is heated by the incandescence of a conducting carbon core, until the salt is volatilised, carrying off most of the metallic impurities as chlorides; the silica is reduced and combines with the excess of carbon present to form silicon carbide. The furnace is 20 feet long, and 1000 horse-power of current is passed through for thirty-six hours.

Charge.

1,000	pounds	carbon in	core.
7,200	,,	,,	,, charge.
12,000	,,	silica	,, ,,
3,000	,,	salt	,, ,,
7,000	,,	silicon carbide formed.	

Assumptions: temperature of furnace 3000° C.; specific heat of carbon 0·5, of silica 0·25, of salt 0·2. Heat of formation of silica = 200,000 calories (per 60 pounds), of carbonic oxide 29.000 calories (per 28 pounds), of silicon carbide small but positive, and assumed as 2000 calories (per 40 pounds). It is further assumed that only the part of the charge actually reduced is heated to the full temperature of the furnace, and the heat going into the unreduced material or packing is not included in the *efficiency*. Reaction assumed—

$$3C + SiO_2 = CSi + 2CO.$$

Heat energy of current: 1000 horse-power for thirty-six hours = 45,620,000 pound calories.

Heat absorbed in heating up part of charge reduced or volatilised: 7300 pounds of carbon = 7300 × 0·5 × 3000 = 10,950,000 calories; 10,500 pounds of silica = 10,500 × 0·25 × 3000 = 7,875,000 pounds calories; in salt volatilised 3000 × 50 = 150,000 calories. Total 18,975,000 calories = 42 per cent of energy of current.

Heat absorbed in chemical reactions: The heat required to split up one molecular weight (60 pounds) of silica is 200,000 calories; the formation of one molecular weight of silicon carbide and two molecular weights of carbonic oxide gives us 60,000 calories, leaving a deficit of 140,000 calories per molecular weight of carbide formed (40 pounds, or 3500 calories per pound of carbide, or 24,500,000 calories for the total 7000 pounds of carbide = 53·5 per cent of the total energy of the current. This value is too high, and the reason is that the heats of formation we have used are those at ordinary temperature, while the reaction takes place at a high temperature with the absorption of less heat. How much less heat is absorbed may be determined by the following considerations:—The amount calculated is the theoretical absorption at ordinary temperatures. It takes 42 per cent of the energy of the current to heat the charge up to the reacting temperature, and yet the products of the reaction, silicon carbide and carbonic oxide, contain much less than that amount of energy as sensible heat; the difference between the heat required to bring the charge up to the reacting temperature and the sensible heat in the products of the reaction at the same temperature, represents the quantity by which the heat absorbed in the chemical reaction has diminished, owing to the higher temperature at which it takes place. Now, the heat in 7000 pounds of silicon carbide is about 7000 × 0·3 × 3000 = 6,300,000 calories; in the 9800 pounds of carbonic oxide 2,200,000 calories, giving a total heat in the products of 8,500 000 calories. Since it took 18,975,000 calories to heat up the charge, the difference, 10,475,000 calories, has disappeared, and has gone towards furthering the chemical reaction. The chemical reaction has therefore absorbed

from outside 24,500,000 − 10,475,000 = 14,025,000 calories = 34·5 per cent of the energy of the current.

Efficiency.—Heating up charge 42 per cent + 34·5 per cent absorbed in the chemical reaction = 76·5 per cent net efficiency.

(To be continued).

PROCEEDINGS OF SOCIETIES.

INSTITUTE OF CHEMISTRY.

The Twenty-fifth Annual General Meeting of the Institute of Chemistry was held at 30, Bloomsbury Square, on Monday, March 2nd, at 4.30 p.m., Professor John Millar Thomson, LL.D., F.R.S., President, in the Chair. The Annual Accounts and the Report of the Auditors having been duly received, Professor Tilden moved the adoption of the Report of the Council, drawing attention to the increase in the members (in spite of heavy losses sustained by death), and also to the increase in the number of candidates for examination, notwithstanding that the Council have, within the last few years, considerably raised the standard of the regulations for admission to the Institute. He also endorsed the warm tribute of appreciation accorded by the Council to the retiring President. Dr. Stevenson seconded the Report, which was then adopted.

Ballot for the election of Censors having been taken, the following were declared elected:—Dr. W. J. Russell, F.R.S.; Dr. Thomas Stevenson, F.R.C.P.; Professor John Millar Thomson, LL.D., F.R.S.; and Professor William Augustus Tilden, D.Sc., F.R.S.

The Meeting proceeded to appoint Auditors, and Messrs. H. Ballantyne, A. R. Ling, and C. H. Cribb were declared elected.

The President then delivered his Address. As the Institute has recently completed a quarter of a century of existence, Professor Thomson submitted a brief history of its work from its foundation to the present time. The Address was divided under definite headings, the first portion being a record of the origin and general progress. The President described how the growing appreciation of the science of analytical chemistry from the utilitarian point of view, led to the necessity for an organisation for maintaining a standard of qualification on the part of analytical and consulting chemists. The real origin of the Institute was a suggestion put forward in 1872, by the late Sir Edward Frankland, at a Dinner given to Professor Cannizzaro on his appointment as Faraday Lecturer. Later, in 1876, he proposed to the Council of the Chemical Society, that a class of Fellows to be styled Licentiates (or some analogous title) should be created for the purpose of distinguishing between competent professional chemists and those who professed an interest in chemistry as a science and not as a means to earning a livelihood. The idea was not adopted, but it was decided to found a new Society, the Institute of Chemistry being formally incorporated under the Companies' Act on October 2nd, 1877.

Among those active in founding the Institnte were mentioned Mr. Carteighe, Professor Hartley, the late Mr. Frederick Manning, Mr. Chas. Tookey, and the late Dr. Alder Wright. Professor Thomson himself was also a keen worker for the Institute in its earliest history. He proceeded to relate its progress under the successive Presidents:—Sir Edward Frankland, Sir Frederick Abel, Dr. William Odling, Dr. James Bell, Professor W. A. Tilden, Dr. W. J. Russell, and Dr. Thomas Stevenson. He dealt with the regulations as to training and examination of candidates for the Associateship of the Institute, showing how the standard of the requirements for membership had been steadily raised, and he commented on the consequent increasing recognition of the qualifications "A.I.C." and "F.I.C." by Government and municipal authorities and by the leaders of industry throughout the kingdom.

After reviewing the Conferences on practising and professional questions held from time to time by the Institute, the President referred to the development of the library, and concluding by expressing his personal satisfaction in the nomination of Mr. David Howard as his successor in the Chair.

The Officers and Members of Council for the ensuing year were then declared elected.

The new President being formally inducted, thanked the Fellows and Associates for the honour bestowed on him, and declared the meeting dissolved.

Officers and Members of Council for the ensuing year:—

President—David Howard.

Vice-Presidents—Walter Ernest Adeney, D.Sc.; George Beilby; Frederick Daniel Chattaway, M.A., D.Sc.; Percy Faraday Frankland, Ph.D., F.R.S.; Francis Robert Japp, LL.D., F.R.S.; John Millar Thomson, LL.D., F.R.S.

Hon. Treasurer—Alfred Gordon Salamon, A.R.S.M.

Members of Council—Leonard Archbutt; Edward John Bevan; Bertram Blount; Horace T. Brown, LL.D., F.R.S.; James Cameron; Charles Edward Cassal; Alfred Chaston Chapman; Edwy Godwin Clayton; Edward Divers, M.D., F.R.S.; James Johnstone Dobbie, M.A., D.Sc.; Bernard Dyer, D.Sc.; Thomas Fairley; Alfred John Greenaway; Henry Wilson Hake, Ph.D.; Henry James Helm; Edward William Taylor Jones; Julius Lewkowitsch, M.A., Ph.D.; William Walker James Nicol, M.A., D.Sc.; Frederick James Montague Page, B.Sc., A.R.S.M.; William Henry Perkin, Ph.D., F.R.S.; William Jackson Pope; Henry Richardson Procter; Percy Andrew Ellis Richards; Alexander Scott, D.Sc., F.R.S.; Joseph Wilson Swan, F.R.S.; Leo Taylor; John Augustus Voelcker, M.A., Ph.D.

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

Ordinary Meeting, March 3rd, 1903.

Mr. Charles Bailey, President, in the Chair.

"*Further Investigation of the Detection and Approximate Estimation of Minute Quantities of Arsenic in Malt, Beer, and Food Stuffs.*" By William Thomson, F.R.S.E., F.I.C.

The author of this paper pointed out that he had greatly improved the process which he had already published (see Chemical News, 1902, vol. lxxxvi., p. 179), and that by this improved method he had been able to obtain a very distinct mirror of arsenic in beer; for instance, when it existed to the extent of $\frac{1}{3000}$th part of a grain per gallon, when working on 50 c.c., which is equivalent to less than a sherry glassful of the beer. This is equivalent to the detection of about one part in two hundred and eighty millions of beer. The refinement in his process depends chiefly on the fact that he heats the naked glass of the tube with a Bunsen flame, the end of which flame heats a piece of copper wire gauze which extends for about a quarter of an inch on to the drawn-out portion of the tube which receives the mirror. Secondly, that the drawn-out portion of the tube is covered with a piece of tissue paper about 1 m.m. distant from the hot wire gauze. The hot wire gauze prevents the formation of a mirror till the liberated arsenic comes in contact with the tube, which is kept cold by a stream of cold water passing over the tissue paper. By this means very minute quantities of arsenic may be easily seen, as they are deposited in a very narrow ring around the cold portion of the tube. He explained the differences which caused the formation of brown metallic mirrors and black arsenic deposits by the subsequent evaporation

of the brown mirrors due to heat, which came in contact with the tube after the brown mirror had been deposited. He showed a method of finding the exact internal diameter of the tube upon which the mirror was to be deposited, and by these combined methods he showed that much greater accuracy could be obtained than hitherto in the estimation of arsenic contained in beer, malt, or food stuffs. He also referred to a curious instance of the fading of mirrors, especially of those which had *not* been formed by the new cooling process when sealed up in an atmosphere of hydrogen. He assumed that this effect was caused by the action of light upon the mirrors.

Professor H. B. Dixon, F.R.S., exhibited an Electrolytic Marsh Apparatus, which had been adopted by the Government authorities for the detection of arsenic, and he claimed that it was sufficiently delicate for the purpose.

Mr. Francis Jones referred to the recent observations on the bending of marble made by Professor See, of Washington, and pointed out that similar phenomena have long been known. Lantern slides were shown of marble tombstones (particularly that of Professor Black) in Edinburgh churchyards, which have fallen to pieces in the course of sixty or seventy years, the marble in each case having bent outwards.

NOTICES OF BOOKS.

A Junior Chemistry. By E. A. Tyler, B.A. London: Methuen and Co. 1902. Pp. 228.

Although many schools are provided with laboratories of a more or less efficient character, the short amount of time that can be set apart for laboratory work prevents most boys learning much practical or experimental work. Lectures by themselves are not of very great use unless they are supplemented by book work and practice. This book is intended to act as that supplement, and will be of much use in assisting the student to acquire a good fundamental knowledge of scientific chemistry.

The first five chapters describe certain physical laws and processes with which the student must be acquainted, such as the properties of matter and their measurement; the influence of temperature and pressure on the volumes of gases; weight and mass, &c. The importance of accurate weighing is insisted on early in the book; and, rightly so, as the value of correct quantitative results cannot be over emphasised. Chapters VI. to X. explain and illustrate the fundamental principles of chemistry, and the remainder of the book is devoted to the study of certain typical elements and compounds.

We are sorry to note the extravagant use the author makes of heavy type and italics; there is not a page where these two methods of emphasis are not used many times. Frequent underlining is always evidence of want of confidence by the writer, who fears that he will not be properly understood; it also gives the book a patchy appearance, and is generally unnecessary.

The Story of Alchemy and the Beginning of Chemistry By M. M. Pattison Muir, M.A. With seventeen illustrations. London: George Newnes, Ltd. 1902. Pp. 185.

Though there is a certain amount of interest in such a book as this, it is not one that should be put in the hands of a young student or beginner, as it would be almost certain to give him, what we know now to be, very distorted ideas on science in general and chemistry in particular.

The story of alchemy is the story of the attempt of philosophers of olden times to account for the material changes they observed, by means of what we might almost call spiritual reasons. In the first place they assumed that all nature was a very simple matter, whereas we know now that it is extremely complex. They attempted to account for the phenomena they observed by the action of four so-called elements—fire, earth, air, and water, with the addition of spirit or essence. "The central quest of alchemy was the quest of an undefined and undefinable *something*, wherein was supposed to be contained all the powers and potencies of life, and whatever makes life worth living . . . it was called the philosopher's stone, the stone of wisdom . . . and many other names were given it." The preceding lines give in a very concise form the principal idea running through all the records of alchemy; perhaps human nature in general is not so very different to-day, the "central quest" is still, as a rule, that of gold.

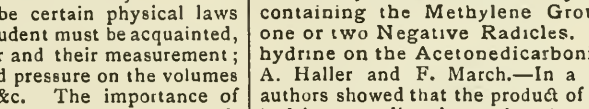
CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

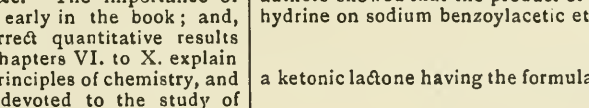
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 7, February 16, 1903.

Law relating to the Electromotive Forces of Piles depending on the Reciprocal Action of Saline Solutions and Soluble Electrolytes.—M. Berthelot.—The author discovers and proves the following law:—When a base acts on an acid, the electromotive force developed is the sum of the electromotive forces developed by the action of the corresponding salt on the acid on the one hand, and on the base on the other hand. The solutions reacting are supposed dilute and equivalent, and causing no separation of gaseous or insoluble products, nor causing any progressive change, other than that of neutralisation, in their interior constitution.

New Syntheses Effected by means of Molecules containing the Methylene Group Associated with one or two Negative Radicles. Action of Epichlorhydrine on the Acetonedicarbonic Sodium Ethers.—A. Haller and F. March.—In a previous research the authors showed that the product of the action of epichlorhydrine on sodium benzoylacetic ether chiefly consists of



a ketonic lactone having the formula



At the same time, MM. Traube and Lehmann showed that epichlorhydrine forms with sodium acetylacetic ether a compound to which they assign an analogous formula. The acetonedicarbonic ethers contain two methylene groups between the negative radicles, and the authors effect a condensation between these ethers and epichlorhydrine.

Conditions under which Manganese in Acid Solution can be Estimated by Persulphates.—H. Baubigny.—When a solution of an alkaline persulphate is heated, this salt loses oxygen, and is transformed into an acid solution by hydration. If such a solution contains manganese, this formation of free acid does not prevent the separation of the metal in the form of peroxide. The author further investigates the subject to find whether, in a previously acidified liquid, this phenomenon is still possible. His experiments were made in the presence of sulphuric acid, nitric acid, also some organic acids. A list of results is given showing the conditions under which the estimation of manganese is possible.

Heat of Formation of certain Sulphur and Nitrogen Compounds.—Marcel Delépine.—Continuing his re-

searches on the sulphur and nitrogen compounds derived from carbon disulphide, the author compares the thermochemical properties of some of these substances. He uses Berthelot's calorimetric bomb; the heats of formation being calculated from the equation of combustion:—

$$C_nH_mN_pS_q + (2n+\frac{m}{2}+3q)O =$$

$$= nCO_2 \text{ gas} + (\frac{m}{2}-q)H_2O \text{ liq.} + pN \text{ gas} + qSO_4H_2 \text{ sol.}$$

Action of Hydrogen on Silver Sulphide in presence of Sulphides of Antimony and Arsenic.—H. Pélabon.—An investigation of the action of hydrogen on various masses of definite mixtures, such as those corresponding to the formulæ $Sb_2S_3Ag_2S$, $Sb_2S_3.3Ag_2S$, $As_2S_3Ag_2S$, $As_2S_3.3Ag_2S$, show that the relation between the partial pressure of sulphuretted hydrogen and the total pressure of the mixed gases (R) increases regularly with the weight of these mixtures.

Action of Phosphoric Acid on Erythrite.—P. Carré.—Phosphoric acid acts on erythrite in the following manner:—(1) Dehydration takes place, and (2) etherification follows, giving a mono-ether of erythran, which substance can further lose another molecule of water, giving at the same time a di-ether resulting from the etherification of the two phosphoric OH groups by a molecule of erythran.

Preparation of certain Combinations of α-Methyl-α'-isopropyladipic Acid.—C. Martine.—The dimethylic and diethylic ethers of α-methyl-α'-isopropyladipic acid are easily prepared by the action of dry hydrochloric acid on a solution of the acid in anhydrous methyl and ethyl alcohols. The author also prepares the diamide, dianilide, and para toluidide of this acid.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 16—17.

Arsenic exists normally in Animals, and is found principally in the Ectodermic Organs.—Armand Gautier.—A controversial paper in which the author defends his previous assertions that arsenic is present in animal organisms.

The Existence of Arsenic in the Organism.—Gabriel Bertrand.—The author upholds M. Gautier's statements that arsenic is present in parts of the animal organism, such as the hair, nails, and skin; he has assured himself that all the reagents used were perfectly free from arsenic, and by repeating M. Gautier's experiments, and making other similar ones, he shows that arsenic is present as stated.

The Detection of very small quantities of Arsenic.—Gabriel Bertrand.—Already noticed.

Alloys of Cadmium and Magnesium.—O. Boudouard.—Already inserted in full.

A Combination of Acetic Acid with Nitric Acid.—Ainé Pictet and P. Genequand.—Already inserted.

The Estimation of Free Anhydrous and Hydrated Lime in Concretes.—M. Maynard.—Already inserted in full.

Action of Isocyanate of Phenyl on the Ethers of some Oxyacids.—E. Lambling.—A continuation of the author's previous papers on the same subject. He describes the action of isocyanate of phenyl on diethyloxalic ether, on benzylic ether, and on salicylate of methyl, and shows that their phenylurethanes do not give the phenylurethanes of the corresponding acids by saponification, but instantly the corresponding anilides according to the equation—

$$\begin{matrix} R_2{=}CO{-}CONH{-}C_6H_5 \\ | \\ CO{-}OH \end{matrix} = CO_2 + \begin{matrix} R{=}COH \\ | \\ CO{-}NH{-}C_6H_5 \end{matrix}.$$

Action of Chlorides and Anhydrides of the Acids of the Fatty Series on Polymerised Methanal.—Marcel Descudé.—Already inserted.

A Method for the Synthesis of Polycyclic Hydrocarbides.—M. Delacre.—To prepare fluorene-carbonic acid, a mixture of one part of trichloracetate of ethyl, ten parts of benzene, and three parts of chloride of aluminium are left at the ordinary temperature for twelve hours; it is then heated on a water-bath so long as hydrochloric acid is given off. Precipitate with water and concentrate the benzenic solution strongly; the addition of ligroïn to the filtered solution causes a fresh deposit of fluorene-carbonic acid. The mother liquors will serve for the preparation of fluorene.

Some Derivatives of β-Naphthylamine.—A. Reychler.—The author describes the preparation and some properties of a number of derivatives of β-naphthylamine; among them are the chlorhydrate of ethyl-β-naphthylamine, the camphor-sulphonate of ethyl-β-naphthylamine, the iodhydrate of diethyl-β-naphthylamine, and some methylised derivatives of β-naphthylamine.

Estimation of Urinary Acidity by Sucrate of Lime.—J. de Girard and J. Vires.—The authors have observed that the addition of sucrate of lime to the solution of monometallic alkaline phosphates gives crystallised bicalcic phosphate. It is concluded that it is this phosphate which is formed by the contact of the two solutions, and that it re-dissolves and remains in solution for a certain time, thanks to the acidity of the solutions. The action of sucrate of lime on the acid phosphates of the alkaline metals can be represented by the following general equation:—

$$nPO_4MH_2 + SCaO = PO_4Ca_2H + PO_4M_2H + (n-2)PO_4MH_2 + SH_2O.$$

Their final conclusion is, however, that sucrate of lime will not serve to determine the acidity of a monometallic phosphate, since the reaction is incomplete to begin with, and it varies with the nature of the metal for the same quantity of phosphoric acid; now urinary acidity is due especially to monometallic phosphates.

New Method of Organic Analysis.—P. Thibault and A. C. Vournasos.—The authors describe a new apparatus for organic analysis and also the method of procedure. The organic matter is, as is usual, burnt with oxide of copper, or with pure peroxide of manganese; they have obtained very good results with various allotropic forms of carbon, as well as with organo-metallic compounds, such as carbonates, oxalates, borates, formates, ferro- and sulphocyanides, &c.

Examination of the Colouring of Animal Fibres by means of Acid Colouring Materials.—P. Sisley.—A long paper not suitable for abstraction.

Mechanism of the Chemical Variations in Plants submitted to the Influence of Nitrate of Sodium.—E. Charabot and A. Hébert.—Already noticed.

MISCELLANEOUS.

Royal Institution.—On Tuesday next (March 17), at 5 o'clock, Sir Robert Ball will commence a course of three lectures at the Royal Institution on "Great Problems in Astronomy"; and on Thursday (March 19), Dr. C. H. Firth delivers the first of three lectures on "Society during the Commonwealth and Protectorate." The Friday Evening Discourse on March 20 will be delivered by Prof. E. A. Schäfer on the "Paths of Volition"; on March 27, by Prof. Herdman on the "Pearl Fisheries of Ceylon"; and on April 3, by Lord Rayleigh on "Drops and Surface Tension."

Sulphide of Cobalt.—W. Herz.—Moist sulphide of cobalt which has not been in contact with the air dissolves in even very dilute hydrochloric acid, whether it has been precipitated hot or cold. When drained it still dissolves in deminormal hydrochloric acid, forming a red solution and giving off sulphuretted hydrogen, but its solubility is much less. If sulphide of cobalt is left for a sufficiently long time in contact with the air, it is transformed partially into sulphate, and consequently loses a portion of its cobalt when shaken up with deminormal hydrochloric acid, or even simply with water. Cobalt will not precipitate with sulphuretted hydrogen on account of the easy solubility of the sulphide in dilute hydrochloric acid. This sulphide, on contact with air, undergoes a transformation (polymerisation) on which the author is at work still.—*Zeit. Anorg. Chemie*, vol. xxvii., p. 390.

Hydroxylamido- and Nitrosoanthraquinones.—L. Wacker.—By reducing 1.2-nitroanthraquinone-sulphonate of sodium in alkaline solution with grape sugar, under the conditions described fully by the author, we obtain 1.2-hydroxylamido-anthraquinone-sulphonic acid, of which the mono-sodic salt is soluble in water, giving a reddish-brown colour, and also the disodic salt, giving a green solution. If we reduce 1.2-nitroanthraquinone-sulphonic acid with sesquioxide of sulphur, we obtain an amido-oxyanthraquinone-sulphonic acid, of which the constitution has been established by its transformation into the green of sulphonised-quinizarine. Now, this same product is formed by the transposition of 1.2-hydroxylamido-anthraquinone-sulphonic acid by means of concentrated sulphuric acid by heating to about 70°—80°. On the other hand, hydroxylamido-anthraquinone-sulphonate of sodium in alkaline solution gives, on oxidation by means of ferricyanide of potassium, nitroso-anthraquinone-sulphonate of sodium.—*Berichte*, vol. xxxv., p. 666.

Oxides of Cobalt.—Erwin Huttner.—Persulphate of potassium gives the following reaction with oxide of cobalt: $2Co(OH)_2 + S_2O_8K_2 + 2H_2O = H_2SO_4 + K_2SO_4 + Co_2(OH)_6$. Other oxides may be formed according to the conditions of the experiment; for example, $3Co_2O_3.5H_2O$ and $Co_2O_3.2H_2O$, analogous to the hydrates given by oxide of iron. With $S_2O_8Am_2$ in acid solution the sesquioxide of cobalt obtained is anhydrous; in alkaline solution we obtain the hydrated oxide. Chlorine and the hypochlorites give an oxide in which the ratio $\frac{O}{Co}$ is decidedly above 1·5.

Oxidation by means of iodine appears, without any doubt, to lead to the formation of a peroxide, CoO_2. Electrolytic oxidation of the salts of cobalt always furnishes sesquioxide. All these oxides dissolve in hydrochloric acid with the evolution of chlorine. The solutions are red when hot, and blue when cold. Nitric and sulphuric acids dissolve them less easily with the evolution of oxygen. With oxalic acid we obtain a green solution, and at the same time carbonic acid is given off. On boiling, the solution takes a yellowish-brown colour, and finally becomes red. Acetic acid dissolves the oxides of cobalt very easily, forming a yellowish-brown solution. This latter is not modified either by the addition of ammonia or of an alkali.—*Zeit. Anorg. Chem.*, vol. xxvii., p. 81.

Quantitative Estimation of Bismuth by Electrolysis.—K. Wimmenhauer.—The author made use of very feeble currents from an accumulator, and measuring instruments by Siemens and Halske, and Hartmann and Braun. His variable resistance was a trough of water with moveable lead plates. The water was made slightly conducting by means of sulphuric acid. The electrolysis was made in the well-known Classen apparatus of about 200 c.c. capacity. The anode consisted of a cylindrical electrode of 70 square c.m. surface, kept in movement by means of a small water turbine. The methods already described do not give very good results, but bismuth is precipitated very nicely (about 0·4 grm.) by using a solution containing from 0·5 to 1 c.c. of concentrated nitric acid for each 0·1 grm. of Bi_2O_3 with a current of 0·05 ampère and 2 volts. The time allowed should be three or four hours, keeping the temperature at about 50°. If we wish to shorten the time of the operation, we can commence with a current of 0·1 ampère, but as soon as the deposit commences to take a brown colour, the current must be reduced to 0·05 ampère. The deposited bismuth must be washed, without interrupting the current, with pure water, then alcohol and ether. If we start with nitrate of bismuth, we can easily effect its solution by making use of a mixture containing two parts of water and one of glycerin. For instance, we take 0·1 to 0·3 grm. of the nitrate and dissolve it in 2 to 4 c.c. of the above mentioned liquid. Dilute to 150 c.c., and electrolyse as described.—*Zeit. Anorg. Ch.*, vol. xxvii., p. 1.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

The Chemistry of the Colouration of Coins.—Could any of your readers kindly tell me whether there are any essays or works dealing with the colourations and characteristics of old coins; or give me any information bearing upon the chemical effects of time or burial in certain earths upon coins, and the possible variations of such effects as determined by the composition of the coins.—S. ARCHIBALD VASEY.

MEETINGS FOR THE WEEK.

MONDAY, 16th.—Society of Arts, 8. (Cantor Lectures). "Hertzian Wave Telegraphy in Theory and Practice," by Prof. J. A. Fleming, M.A., D.Sc., F.R.S.

—— Society of Chemical Industry, 8. "The Standardisation of Analytical Methods," by H. Droop Richmond, F.I.C., F.C.S. "The Standardisation of Commercial Methods of Analysis, especially those applied to Brewing Materials," by Arthur R. Ling, F.I.C., F.C.S.

TUESDAY, 17th.—Royal Institution, 5. "Great Problems in Astronomy," by Sir Robert Ball, F.R.S.

—— Society of Arts, 4.30. "Artistic Fans," by Miss Hannah Falcke.

WEDNESDAY, 18th.—Society of Arts, 8. "New Aspects of Life Assurance," by William Schooling.

—— Microscopical, 8. "The Helmholtz Theory of the Microscope," by J. W. Gordon.

—— Chemical, 5 30. "Essential Oil of Hops" and "On a Compound of Dextrose with Hydroxide of Aluminium," by A. C. Chapman. "Action of Phosphorus Haloids on Dihydroresorcins—Part II., Dihydroresorcin," by A. W. Crossley and P. Haas. "On the Constitution of Cotarnine," by J. J. Dobbie, A. Lauder, and C. K. Tinkler. "Decomposition of Mercurous Nitrite by Heat," by P. C. Ray and J. N. Sen.

THURSDAY, 19th.—Royal Institution, 5. "Society during the Commonwealth and Protectorate," by Charles Harding Firth, M.A.

FRIDAY, 20th.—Royal Institution, 9. "The Paths of Volition," by Prof. E. A. Schäfer, LL.D., F.R.S.

SATURDAY, 21st.—Royal Institution, 3. "Light—its Origin and Nature," by Lord Rayleigh, F.R.S., &c.

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Offices of the School, Suffolk Street,
March 3rd, 1903.

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THE CHEMICAL NEWS

Vol. LXXXVII., No. 2260.

ON POLONIUM.

By F. GIESEL.

The small quantities of bismuth which may be obtained from the lead separations of the uranium minerals (*Berichte*, 1900, xxxiii., 1667), at first emit penetrating (β) rays, to about the same extent as a barium salt containing about 5 per cent of radium. It is already known that after some time these rays gradually disappear, until only a residual effect remains. I have shown (*Berichte*, 1902, xxxv., 3610) that from such bismuth Marckwald's substance may be derived, which only yields the (α) rays which can be absorbed.

It was interesting to observe whether also the method of purification described by Mdme. Curie (*Physik. Zeit.*, 1903, viii., 234) for her polonium might be used with the same result as Marckwald's method on my fresh polonium. This is actually the case. If, for example, the hydroxide is treated with a sufficient excess of nitric acid, sometimes a small quantity of yellowish flakes remains undissolved; these phosphoresce, and only give α-rays. From the filtrate, by repeated fractional precipitation with water, bismuth sub-nitrate may be obtained, and the most difficultly soluble fractions become more and more like Marckwald's substance; the precipitates from the mother-liquor, on the contrary, give finally only β-rays. Fractional precipitation with metallic magnesium acts similarly. If the chloride is evaporated to dryness on the water-bath the mass becomes blackish, and on solution in hydrochloric acid brownish-black flakes remain undissolved; these emit α-rays very strongly. But the separations are not so complete as when Marckwald's beautiful method with metallic bismuth* is employed. If a fragment of bismuth is placed in a solution of the chloride previously purified by Curie's method, even after some days no trace of a precipitate appears, and no colouration can be perceived on it. The effect is all the more surprising. The piece of bismuth phosphoresces, ozonises the air, and when it is placed on the zinc sulphide screen the immediate surroundings radiate as strongly as the barium platinum cyanide screen owing to pure radium.

If older preparations of polonium are examined in the same way the same results are obtained, but the products are of less value. This leads me to the supposition that the α-radiation also of the substance is not constant.

I have not demonstrated the presence of tellurium, nor yet succeeded in purifying the substance with zinc chloride. Nor have I been able to observe anything which would suggest that the polonium preparations (with α-radiation) prepared by different methods are not qualitatively identical; they only differ quantitatively owing to varying adulteration with inactive substances, or with those rendered active by induction (bismuth).

I might mention that the two separations of my polonium, whose rays are called α- and β-rays respectively, may be distinguished by the aid of the zinc sulphide screen and the ordinary barium platinum cyanide screen.† The α-radiation only acts on the former, and the β-radiation on the latter.

The β radiation of radium behaves differently, for it affects both screens.—*Berichte der Deutsch. Chem. Ges.*, 1903, xxxvi., 728.

* Similar results may be obtained in less degree with platinum and gold, and better with palladium than with bismuth; but it is questionable whether analogous reactions occur.

† An unvarnished barium platinum cyanide screen is also affected by the α-radiation, but the zinc sulphide screen is far more sensitive.

THE REDUCTION OF VANADIC ACID BY THE ACTION OF HYDROCHLORIC ACID.*

By F. A. GOOCH and L. B. STOOKEY.

Bunsen (*Liebig's Ann. Chem.*, xcvi., 265) and Mohr ("Titrirmethode," v. Aufl., 314) have proposed to estimate vanadic acid by the action of concentrated aqueous hydrochloric acid, thus reducing it from the condition of oxidation represented by the pentoxide to that of the tetroxide, in accordance with the equation—

$$V_2O_5 + 2HCl = V_2O_4 + H_2O + Cl_2,$$

and determining iodometrically the chlorine evolved.

In an attempt by Czudnowicz (*Ann. Phys.*, cxx., 17) to make use of this reaction by collecting in standard arsenious acid the chlorine evolved from the boiling mixture of hydrochloric acid and vanadic acid, and titrating the excess of the arsenious acid by iodine, accordant results were not obtained. On the other hand, Gibbs (*Proc. Amer. Acad.*, x., 250) was able to determine with a fair degree of accuracy the small amounts of vanadium pentoxide found in the vanadio-tungstates and other complex combinations, by boiling with strong hydrochloric acid, collecting in potassium iodide the chlorine evolved, titrating the freed iodine with sodium thiosulphate, and calculating from the amount of iodine thus found the vanadium pentoxide corresponding to a change of condition from V_2O_5 to V_2O_4.

Milch (Inaug. Dissert., Berlin, 1887, 10) was unable to substantiate the work of Gibbs, and, obtaining in four experiments, upon approximately 0·2 grm., 0·5 grm., and 1·0 grm. of vanadium pentoxide, amounts of chlorine varying with the quantity of material handled, and never exceeding one-fourth of the amount demanded by theory, was led to suppose that the degree of reduction was not constant, being larger in proportion as the quantity of pentoxide used was smaller. Milch concluded that while accordant results might be obtained by working with approximately similar amounts of material, the process afforded no ground for the calculation of the actual amount of pentoxide present.

Rosenheim (Inaug. Dissert., Berlin, 1888; *Liebig's Ann. Chem.*, ccli., 197) also tested the process, working with pure vanadates and pure vanadium pentoxide. Concentrated hydrochloric acid, of sp. gr. 1·19, was employed, and care was taken to dry the distillation flask before introducing the materials, because even slight dilution of the acid lessened the evolution of chlorine in marked degree. Three stages were noted in the action of hydrochloric acid upon vanadic acid. The vanadic acid first dissolved to a solution of a deep brown colour without perceptible evolution of chlorine; upon warming, the solution suddenly evolved chlorine and took on a deep green colour; thereafter the evolution of chlorine became weaker, and the solution, giving off a small amount of chlorine on strong boiling, assumed a clear blue colour. After this, further heating effected no change. It is recommended to raise the temperature gradually, in order that the acid may not boil over into the receiver, and to keep this receiver cool so that iodine may not be volatilised by steam from the flask during the prolonged heating. In the experiments with ammonium vanadate, in which the heating was interrupted after the first violent evolution of chlorine, the iodine found in the receiver indicated, according to Rosenheim's figures, about 50 per cent of the vanadium pentoxide present; in three experiments longer continued, the indications advanced about 6 per cent; and in three experiments continued presumably to the end—to the appearance of this blue colour—the amounts of pentoxide indicated were 61·77 per cent, 63·71 per cent, 61·89 per cent of the quantities actually taken, and further heating with another receiver until

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, vol. xiv., No. 83.

almost all the hydrochloric acid had been volatilised, resulted in no further progress in the reaction. Experiments with potassium vanadate and with vanadium pentoxide resulted similarly. Rosenheim draws the inference that a titrimetric method based upon a theory of reduction from V_2O_5 to V_2O_4 by the action of hydrochloric acid must lead to false conclusions, and suggests that his results lend probability to the supposition that an oxide of the formula $(V_2O_4)_2V_2O_5$ is formed, although the actual reductions observed by him are not quantitatively in accord with the formation of such a body—which implies a reduction covering about 66 per cent of the interval between V_2O_5 and V_2O_4. Rosenheim concludes that the whole method is to be rejected in quantitative estimations. An inspection of Rosenheim's tables, however, shows that the standards of the solutions of thiosulphate and iodine have been interchanged either in the printed record or in the calculation of results. In the latter event, the actual indications of the process would be about 15 per cent higher than Rosenheim's figures, but still approximately 20 per cent below the theory of the reduction from V_2O_5 to V_2O_4.

In Holverscheit's hands the process gave results most irregular and unsatisfactory (Inaug. Dissert., Berlin, 1890). Ammonium vanadate was the material taken for the experiments, and the residue obtained by treating this salt with potassium hydroxide and evaporating to expel ammonia, was boiled in a Bunsen distillation apparatus with concentrated hydrochloric acid. The solution, at first yellow, became green on long boiling. In some cases ebullition was kept up for fifteen minutes. In working with amounts of material represented by 0·0585 grm., or 0·1171 grm. of V_2O_5, Holverscheit obtained from about 28 per cent to 39 per cent—or, in the average, about a third of the theoretical reduction—and, while noting the fact that by working with wholly concentrated ("ganz. konz.") HCl Rosenheim doubled this yield, ventures the opinion that it is scarcely conceivable that Gibbs obtained by boiling vanadic acid with hydrochloric acid and estimating the chlorine liberated, results even approximating the truth.

The green colour of Holversheit's residual solution shows, of course, an incomplete reduction—the consequence of the use of an acid which, as intimated, was not of full strength. Rosenheim, however, got the blue residual solutions characteristic of the condition of oxidation corresponding to V_2O_4. Why the deficiency in the chlorine indicated in the receiver in Rosenheim's experiments was so marked is not obvious, unless it be supposed that chlorine was lost from the apparatus in the sudden evolution which takes place when action begins. Our experience, moreover, shows that the liberation of chlorine begins as soon as the hydrochloric acid and vanadic acid come into contact. In our experiments upon the process, therefore, we have used a form of apparatus such that no chlorine can be evolved before the apparatus is connected and ready. For the retort we have used a Voit flask upon the inlet tube of which was sealed a stoppered funnel, while the outlet tube was sealed to a Drexel wash-bottle, and this in turn was joined to Will and Varrentrapp bulbs. The Drexel bottle and bulbs used as receiver and trap were charged with water containing 3 grms. of potassium iodide; the vanadate was introduced into the dry flask, and the apparatus was adjusted. Hydrochloric acid was put in the stoppered separating funnel and, when all was ready, allowed to run into the flask. Connection was made between the funnel and a carbon dioxide generator, so that by passing carbon dioxide through the apparatus all danger of regurgitation might be avoided. Sometimes in the course of our work, too, a branched connection with the funnel tube was so arranged that either hydrochloric acid gas or carbon dioxide, or both, might at pleasure be sent into the apparatus. We have used in the experiments to be detailed ammonium vanadate either purchased in pure condition or made by precipitation with alcohol, or prepared from the oxychloride obtained by acting with chloroform upon ignited vanadium pentoxide. In each case the content in vanadium pentoxide was determined by ignition and confirmed by Holverscheit's bromide process (Inaug. Dissert., p. 48).

In Table I., A, are gathered results obtained by the use of the ordinary pure hydrochloric acid of the laboratory of sp. gr. 1·17; while in B of the same table are recorded results got by using acid of sp. gr. 1·20, specially prepared by saturation of the former acid, kept cold by ice, with hydrochloric acid gas.

In these experiments, in which the precautions described to catch all the chlorine evolved were taken, the actual registration of chlorine amounts in the average to 92·62 per cent of the theory when the ordinary pure acid of the laboratory of sp. gr. 1·17 was used, and to 94·46 per cent when the specially concentrated acid of sp. gr. 1·20 was employed. While the error of these determinations would amount to a considerable figure when large amounts of vanadic acid are to be determined, it is obvious that a correction of, let us say, 6 per cent or 8 per cent upon the small proportions of vanadium pentoxide present in many of the complex salts to which Gibbs applied this method, would not change the significance of the analysis. Indeed, reference to the original shows that the formulæ deduced by Gibbs would in many cases apply as well to the corrected results as to the original figures. Thus it appears that, so far as concerns the special cases, in which Gibbs used this method of analysis, the conclusion of Milch that the process affords no ground for the calculation of the amounts of pentoxide present, and Holverscheit's difficulty in supposing that results were even approximately true, prove to be unfounded, while Rosenheim's suppositious oxide disappears.

In the light of these results it is of interest to note the effect of a repetition of this treatment with strong acid of the residue of the first action weakened by boiling. Plainly two methods of bringing about the re-treatment with strong acid are open: either the weak acid remaining after the boiling process may be wholly removed by evaporation and replaced by concentrated acid, or it may be cooled and re-saturated with gaseous acid. Table II. contains the record of results obtained in both these ways.

These experiments show very clearly that several successive treatments with strongest hydrochloric acid, consisting either in the addition of the concentrated aqueous acid to the dry residue in successive portions, or in passing gaseous acid through the residual liquid cooled in ice-water, finally bring the residue to a condition of reduction in which the re-charging of the liquid residue with gaseous acid produces no brown or green colour, but a clear blue. When this condition is reached the Holverscheit procedure produces no appreciable further reduction. The holding of the blue colour when the solution cooled in ice-water is thoroughly charged with the gaseous acid, appears to be the best evidence of the complete reduction of V_2O_5 to V_2O_4; it is not sufficient that the boiled solution, in which the acid has been weakened, should be blue.

In the several manipulations of the repeated processes there is likely to be some mechanical loss of chlorine. For this reason, the direct titration of the residues by potassium permanganate in presence of a manganous salt was combined, as a control, with the determinations of the iodine set free by chlorine in the distillate, as shown in the experiments of Table III.

In these experiments we have again evidence that it is possible to effect the reduction of vanadic acid to within a few per cent of the amount present by a single treatment with concentrated hydrochloric acid, and that the amount of the reduction may be determined by titrating the residue with potassium permanganate. It is plain, therefore, that Gibbs's application of this mode of reduction and titration to the determination of the small proportions of vanadium pentoxide found in many of the complex salts studied by him is also justified.

The experiments show also that when the action of hydrochloric acid is sufficiently continued, ordinarily large

Table I.

NH_4VO_3 taken. Grm.	HCl taken. C.m.³.	V_2O_5 by calculation. Grm.	V_2O_5 found. Grm.	Error in terms of V_2O_5. Grm.	Per cent.	Details of treatment.
			A.			
0·0500	20 (sp. gr. 1·17)	0·0387	0·0348	0·0039	10·08	Boiled five minutes to blue colour.
0·1000	40 ,, ,,	0·0765	0·0709	0·0056	7·32	
0·1000	40 ,, ,,	0·0765	0·0714	0·0051	6·67	
0·1000	40 ,, ,,	0·0765	0·0705	0·0060	7·84	
0·3000	30 ,, ,,	0·2295	0·2125	0·0170	7·41	Boiled to blue colour.
0·3000	25 ,, ,,	0·2295	0·2179	0·0116	5·06	
			B.			
0·1000	30 (sp. gr. 1·20)	0·0765	0·0716	0·0049	6·41	Boiled to blue; brown when re-saturated.
0·1000	30 ,, ,,	0·0765	0·0732	0·0033	4·31	
0·1000	30 ,, ,,	0·0765	0·0734	0·0031	4·05	
0·1000	30 ,, ,,	0·0765	0·0734	0·0031	4·05	
0·1000	25 ,, ,,	0·0765	0·0711	0·0054	7·06	
0·1000	25 ,, ,,	0·0765	0·0709	0·0056	7·32	

Table II.

NH_4VO_3 taken. Grm.	HCl taken. C.m.³.	V_2O_5 calculated. Grm.	V_2O_5 found. Grm.	Error. Grm.	Details of treatment.
0·1000	10 (sp. gr. 1·20)	0·0752	—	—	Evaporated to dryness. Residue brown when treated with concentrated HCl.
	5* ,, ,,	0·0752	—	—	
	5* ,, ,,	0·0752	0·0737	0·0015	
0·1000	40 ,, ,,	0·0752	0·0700	0·0052	Boiled fifteen minutes.
	—	0·0752	—	—	Evaporated to dryness. Residue treated with KBr gave Br equivalent to 0·0001 V_2O_5.
	7* ,, ,,	0·0752	—	—†	
	7* ,, ,,	0·0752	—	—†	
	7† ,, ,,	0·0752	0·0742	0·0010†	
0·1000	40 ,, ,,	0·0752	0·0699	0·0053* (*a*)	Boiled—(*a*) twenty minutes, (*b*) five minutes, (*c*) five minutes. Residue blue with concentrated HCl or with KBr gave Br equivalent to 0·0004 V_2O_5.
	Gas‡	0·0752	0·0733	0·0029† (*b*)	
	Gas†	0·0752	0·0751	0·0001† (*c*)	

* Brown. † Blue. ‡ Green.

Table III.

NH_4VO_3. Grm.	Aq. HCl. C.m.³.	V_2O_5 calculated. Grm.	V_2O_5 found by chlorine in distillate. Grm.	Error. Grm.	V_2O_5 found by $KMnO_4$ as residue. Grm.	Error. Grm.
0·1000	25 (sp. gr. 1·20)	0·0765	—	—	0·0740 (*a*)	0·0025 −
0·1000	25 ,, ,,	0·0765	—	—	0·0736 (*a*)	0·0029 −
0·1000	25 ,, ,,	0·0765	—	—	0·0744 (*a*)	0·0021 −
0·1000	30 ,, ,,	0·0765	0·0711	0·0054	— (*a*)	—
	Gas (*c*)	—	0·0734	0·0031	0·0758 (*b*)	0·0007 −
0·1000	25 ,, ,,	0·0765	0·0714	0·0051	— (*a*)	—
	Gas (*c*)	—	0·0746	0·0019	— (*a*)	—
	Gas (*c*)	—	0·0765	0·0000	0·0765 (*b*)	0·0000
0·3000	25 ,, ,,	0·2295	—	—	— (*a*)	—
	Gas (*c*)	—	—	—	— (*a*)	—
	Gas (*c*)	—	—	—	0·2284 (*b*)	0·0011 −
0·3000	25 ,, ,,	0·2295	0·2259	0·0036	— (*a*)	—
	Gas (*c*)	—	0·2288	0·0007	0·2302 (*b*)	0·0007 +
0·3000	25 (sp. gr. 1·17)	0·2295	0·2207	0·0088	— (*a*)	—
	Gas (*c*)	—	0·2244	0·0051	— (*a*)	—
	Gas (*c*)	—	0·2258	0·0037	— (*a*)"	—
	Gas (*c*)	—	0·2269	0·0026	— (*a*)	—
	Gas (*c*)	—	0·2281	0·0014	0·2293 (*b*)	0·0002 −

(*a*) Residue after boiling was blue.
(*b*) Residue blue after boiling was still blue when re-saturated.
(*c*) Residue was cooled in ice-water and re-saturated with gaseous HCl.

amounts of vanadic acid may be completely reduced to the condition of the tetroxide; and the method of reduction is of special advantage in those cases which call for titration of the tetroxide by permanganate, since in such cases the use of Holverscheit's admirable method of reduction by hydrobromic acid is precluded.

THE EFFICIENCY OF ELECTRIC FURNACES.*

By JOSEPH W. RICHARDS.

(Concluded from p. 128).

Heating with Fusion and Chemical Reaction.

THERE are numerous instances of this kind of electric furnace operations, in which, particularly, reductions to metal or other metallic compounds are operated. The United Barium Co.'s process is a good instance, barium sulphate being mixed with a small amount of carbon and the charge reduced to a mixture of barium sulphide and oxide in the electric furnace. The calculations, however, are complicated by the fact that the chemical reaction absorbs very much less heat at the furnace temperature than that calculated at the ordinary temperature, as is known from the fact that the efficiency calculated without reference to that factor runs over 100 per cent. The specific heat of the product is unknown, as well as its composition being variable, so that it is impossible at present to allow for the correction required.

The production of calcium carbide presents some interesting data, and may be employed to illustrate this class of operations. Assuming an output of 4 tons per 1000 horse-power per day, or 250 horse-power days per ton, the temperature 2750° C., and using the heats of formation at ordinary temperature, we have:—

Heat energy of current, 250 horse-power per day = 7,200,000 pound calories.

Absorbed in heating charge, 2000 pounds of lime = $2000 \times 0{\cdot}25 \times 2750 = 1{,}375{,}000$ calories; 1500 pounds of coke = $1500 \times 0{\cdot}5 \times 2750 = 2{,}062{,}500$. Sum, 3,437,500 calories.

Absorbed in chemical reaction:—In the formation of 64 parts of carbide, the heat balance is as follows:—

Decomposition of 56 parts of lime ..	—	130,500 cals.
Formation of 64 parts of carbide.. ..	—	7,250 ,,
Heat absorbed..	—	137,750 ,,
Formation of 28 parts carbonic oxide ..		29,400 ,,
Net heat absorbed	—	108,350 ,,
Absorbed per unit of carbide		1,690 ,,
Absorbed per ton of carbide		3,380,000 ,,

This figure may be too high, like that calculated for formation of carborundum, but we do not have the data to make further corrections. The sum total of the heat required to heat up the charge and that absorbed in chemical reactions is 6,817,500 calories, or nearly 95 per cent, which is certainly too high. An assumption of a probable value for the specific heat of the carbide would change the figures materially, making the heat absorbed in the reaction only 14 per cent of the whole heating effect, which added to the 48 per cent required to heat up the charge gives a net efficiency of 62 per cent.

There is a distinct experimental gap in the lack of knowledge of the specific heat of these products of the electric furnace at high temperatures. When these are known, our calculations can be made with much greater exactness.

The net result, however, seems to point to a commercial efficiency of 60 to 75 per cent, calculating, as I have indicated, with furnaces of 200 to 1000 horse-power. The value of such an approximate figure is, that any one starting an electric furnace operation should be able to calculate the approximate output to be expected; or, if planning or designing for a given output, will have a guide to indicate the approximate size and capacity of the furnaces needed.

I have left out of consideration the cases where electrolysis takes place, using fused electrolytes, because in these the production is proportional to the ampères of current used, and not to the total energy of the current, and can be operated only with direct current. Such are essentially strictly electrolytic processes, in which the heating effect of the current is unavoidable and incidental to the main process of electrolysis, and such must be excluded from the term "electric furnace processes" if that term is to retain its individuality and stand for a definite class of operations.

The considerations of such electrolytic operations on fused salts may be carried out in a similar manner to the above calculations, using the energy absorbed in the electrolytic decomposition and secondary reactions as energy rendered latent and utilised. I have worked out, as an example, the electrolysis of fused sodium chloride by the Acker process as follows:—

8200 ampères are passed through a pot electrolysing 36·5 pounds of sodium chloride per hour. The drop of potential is 6·5 volts, of which 3·5 are absorbed in electrolytic decomposition. We can therefore say at once that $\frac{3{\cdot}5}{6{\cdot}5} = 54$ per cent of the energy of the current is usefully applied to decomposition of the electrolyte. In addition to this 36·5 pounds of salt must be melted per hour. The whole energy of the current, 8200 ampères by 6·5 volts drop, is equal to 85,300 pound calories per hour. The salt requires the following heat per pound to melt it and bring it to 850°.

To bring to melting-point 775°, $0{\cdot}25 \times 775$	=	143·5 cals.
Latent heat of fusion..	=	40·0 ,,
To bring up to 850°, $0{\cdot}3 \times (850-775)$ ..	=	22·5 ,,
Total per pound of salt	=	206 0 ,,
Totol per 36·5 pounds of salt	=	7,519 cals.

This quantity is therefore $\frac{7{,}519}{85{,}300} = 9$ per cent of the total heat of the current.

Efficiency.—The sum of 9 and 54 gives 63 per cent of the energy of the current usefully applied; the other 37 per cent is lost by radiation. Of the total heat actually generated by the resistance of the electrolyte, $9 \times \frac{6{\cdot}5}{3} = 19{\cdot}5$ per cent is absorbed in melting the freshly added salt, and 80·5 per cent is lost by radiation and in the hot products.

Discussion.

Mr. CARL HERING—Mr. Chairman, I am glad that Professor Richards has called attention to this important term, efficiency, because it seems to me that it is often used very loosely, and unless there is an explanation of what is meant by the term in any particular case, the figures will mean absolutely nothing, or almost nothing, because the term efficiency can be applied to various stages of the process. The proper meaning of efficiency is the actual divided by the theoretical amount of energy, but the trouble with furnaces is that frequently we do not know what the theoretical amount is. In many cases it has not been determined, and in other cases it has been determined only roughly. I believe I am correct in saying that for calcium carbide the actual figure is not yet definitely known, unless it has been determined very recently. There is another way in which the efficiency of a furnace can be stated, in which it is perfectly safe to use the term, namely, to say that the efficiency of a certain furnace is so-and-so many pounds of the final pro-

* A Paper read at the Second Meeting of the American Electrochemical Society, Niagara Falls, N.Y., September 15th, 1902. From the *Transactions of the American Electrochemical Society*, II., p. 51.

duct per kilowatt hour. This is, perhaps, a loose way of using the term efficiency, but it is a practical way, and whenever the theoretical figures are not known, it seems to me that it affords a very good way of stating the efficiency of furnaces when you want to compare different ones for doing the same work. This use of the term is analogous to its use in connection with incandescent lamps; there also we do not know the theoretical light equivalent, so we speak of the efficiency of an incandescent light as being so-and-so many candles per watt, or watts per candle.

Much can often be learned if we analyse the efficiencies of various parts of the process in a furnace. In many cases heat is actually absorbed in the formation of the compound, as, for instance, in the formation of calcium carbide heat is absorbed, so to speak; that is, energy is being stored up in the final product. This is a very important factor in calculating efficiencies.

There is one term in connection with the measurements of the efficiency of certain furnaces which it is very difficult to include, because one cannot measure or calculate it. It occurs in resistance furnaces in which the current passes through the material itself, and is due to the loss by the conduction of current through the lining of the trough, which is generally fire-brick. It is known that fire brick at a certain temperature will conduct current; that this is a leakage current which causes no electrolysis of the compound but merely supplies heat; the trouble is, that one cannot measure or calculate the amount.

Prof. W. D. Bancroft—If I understood Professor Richards rightly, it appears that he counts in the heat of fusion in making his calculations in regard to efficiency. Now, the heat of fusion, of course, is a factor in considering the length of time necessary for the furnace to heat up to the equilibrium temperature under a given current, but it does not seem to me that it has anything to do with the final temperature that has been reached, because that final temperature is simply a question of the actual radiation at that temperature; the mass is fused, and the amount of heat necessary to fuse it does not come in in determining the equilibrium temperature.

Prof. Hart—Mr. Chairman, I would like to call attention to one fact. We start out in the application of electric energy with a tremendous handicap, where it is not made, as here, by water-power. In many cases it cannot be made by water-power. Take nitric acid: it is impossible to transport nitric acid cheaply a long distance. It is necessary, therefore, to make it on the spot. You cannot get the water-power, for example, in Pittsburg, and there you start in with a tremendous handicap. This is a question which will well bear very thorough investigation, because upon the successful utilisation of collectible energy where a high percentage of the energy is obtained, largely depends the future of electricity.

Mr. Whitney—Mr. Chairman, I should like to learn, if possible, what experiments have been made to reduce this loss of approximately 40 per cent of the energy, which, as I understand it, is the loss through radiation, as I am interested in knowing how much that may possibly be reduced by building the retaining walls of the furnace in such a way as to leave small air chambers throughout the wall.

Dr. Haber—I am interested in learning what numbers you use for the output of calcium carbide; what number of killowatt hours do you use in the calculations per ton of carbide produced?

Prof. Richards—I would say in reply to Mr. Hering, that the term efficiency has two meanings, according to whether it is a continuous operation or a discontinuous one. That is, it may have two shades of meaning. In a continuous operation it represents the melting of the substance added and that absorbed in chemical decomposition. The relation of those two factors to the total would be the efficiency. In a discontinuous operation like the manufacture of graphite, you have simply the heating-up of the material to the final temperature. What heat is radiated after the operation stops, in a discontinuous operation, I would account as heat which had been usefully applied, and not as radiated heat that is totally lost, whereas in a continuous operation all that is lost by radiation is a total loss.

In the manufacture of calcium carbide I have taken a production of four tons per day per thousand horse-power as the basis of my calculation.

With regard to the loss in the lining of the furnace, that was illustrated in the loss in the packing around articles to be graphitised. For instance, the current is passed through the articles to be graphitised, but they must be covered up with a heat insulating material in order to bring them up to a proper temperature, and the lining of the furnace, if the packing may be so-called, in that case absorbed, I think, 30 per cent of the energy of the current. But in the case of the current passing through the substance itself, and not through the lining, as in the case of a non-conducting lining, that amount, I think, is usually small. The conductivity of the charge increases greatly with the high temperature, more rapidly than the conductivity of the lining, which is not heated to so high a temperature, and the ratio of the current going through the charge to that going through the lining is, in my experience, large. In one furnace on which I made experiments and calculations, 96 per cent of the current went through the charge material, while only 4 per cent went through the lining of the furnace. In regard to Professor Bancroft's remark about the heat of fusion in the continuous operation, for instance in the Acker process, where salt is continually added in solid form, it has to be heated, melted, and brought up to the temperature of the furnace, and its latent heat of fusion as well as its specific heat in the solid and liquid stages, will have to be brought into the calculation in order to get the total heat used for liquefying the materials charged.

The idea has often come to me, as to an electric furnace, to look at it as if it were Pegasus hitched to a cart. You have a source of very intense and high temperature, but you can keep that temperature down by regulating the supply of materials, and the temperature can be kept within moderate limits by a rapid charging and discharging of materials from the furnace, so that it is quite possible to conduct an electric operation at ordinary furnace temperature, keeping it down by simply putting a load on it; that is, by charging and discharging the furnace rapidly. I think that principle can be made use of with very fruitful results in chemical operations which we want to take place at a comparatively low temperature.

Replying to Mr. Whitney, I have no experience with regard to making walls hollow or attempting to reduce the radiation in that way. I think the increase of the size of the furnace, where practicable, is the far better way of decreasing relatively the amount of radiation, increasing the size of the furnace and the rate at which the furnace works, and you thus decrease relatively very rapidly the amount of heat lost by radiation. It is like working a steel furnace fast or slow. By working a furnace fast you can reduce the relative amount of loss by radiation and increase the efficiency very greatly.

Pure Iodine.—A. Ladenburg.—Pure iodine, for the determination of the atomic weight, was prepared in the following manner:—Precipitated iodide of silver was left to digest for twenty-four hours with concentrated ammonia, to remove all traces of chloride or bromide of silver, and then by means of zinc it was converted into iodide of zinc, and the iodine, extracted from this latter by means of nitrous acid, was distilled in a current of steam. The iodine prepared in this manner appeared to be a little blacker and less volatile than ordinary iodine; it boiled at 183·5°, fused at 116·1°, and its specific gravity was 4·933.—*Berichte*, vol. xxxv., p. 1256.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, March 5th, 1903.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

MESSRS. Brincker, Howorth, Beanes, J. E. Mackenzie, Cousins, and Desch were formally admitted Fellows of the Society.

The lists of names of the Officers and Council proposed for Election by the Council were read from the Chair.

Certificates were read for the first time in favour of Messrs. Henry Guest Adshead, Heysham, Wimbledon Park, Wimbledon; Harford Montgomery Atkinson, 32, Bagnall Road, Milton; George Neville Blackshaw, Agricultural College, Aspatria; Harry T. Calvert, D.Sc., West Riding of Yorkshire Rivers Board; Ben Caudwell, B.A., 28, Wigfull Road, Sheffield; Alan Fletcher, 132, Holland Road, Kensington, W.; Arthur Ernest Pitt, 66, Abbot Road, Bromley, E.; Harold Russell Pitt, 8, Church Lane, Charlton, S.E.; Frederick Robertson, The Hewan, Bearsden, Glasgow; Fitzroy Owen Jonathan Roose, Oxford Road, Bournemouth; Henry Edward Stevenson, 5, Turner's Road, Bow, London, E.; James Bates Wilkinson, M.D., Town Hall, Oldham.

Of the following papers, those marked * were read:—

*31. "*The Mechanism of the Reduction of Potassium Bichromate by Sulphurous Acid.*" By H. BASSETT, jun.

Berthier, who investigated the action of sulphur dioxide on solutions of potassium bichromate and potassium chromate (*Ann. Chim., Phys.*, 1843, [iii.], vii., 77), stated that in both cases a mixture of sulphate and dithionate was formed, but without giving details.

The reaction has now been studied more fully, and the results show that 94—95 per cent of sulphate and 5—6 per cent of dithionate are formed, when potassium bichromate, potassium chromate, or chromic acid is reduced by sulphurous acid; the amount of dithionate produced being independent of the temperature.

Solutions containing known amounts of sulphurous acid and potassium bichromate were mixed, and the excess of sulphurous acid estimated with iodine and sodium thiosulphate, or the excess of chromate determined by means of ferrous ammonium sulphate.

The freshly reduced solutions do not give the reactions of either chromium or SO_4, and seem to contain a compound—

$$\left.\begin{matrix}KSO_3\\KSO_4\end{matrix}\right\rangle Cr_2(SO_4)_2$$

(or the corresponding acid), which slowly decomposes into $Cr_2(SO_4)_3$ and K_2SO_3.

When sulphuric acid or potassium sulphate is added to these solutions, it enters into combination in such a way that the reactions of SO_4 are not given by the resulting mixture, and as many as 6 mols. of sulphuric acid may be taken up by 1 mol. of chromium sulphate.

Electrolytic experiments show that the green solutions contain a green anion, which slowly decomposes into violet chromium and SO_4 ions.

*32. "*The Constitution of Pilocarpine.*" Part IV. By H. A. D. JOWETT.

The author showed that the constitutional formula for pilocarpine, suggested by Pinner and Schwarz, is only one of several equally probable on the results hitherto recorded.

The constitution of *iso*pilocarpine has, however, been determined by a study of the reactions of dimethylglyoxaline and dimethylpyrazole and by the formation of 1-methylglyoxaline, 1 : 4(or 1 : 5)-dimethylglyoxaline, 1 : 4(or 1 : 5)-methylamylglyoxaline, and probably 1 : 4 (or 1 : 5)-methylamyleneglyoxaline, together with ammonia and methylamine, when the alkaloid is distilled with soda lime.

Dimethylglyoxaline, from *iso*pilocarpine, boiled at 210—215° and formed crystalline salts; *platinichloride*, m. p. 238—239°; *aurichloride*, m. p. 214—215°; *picrate*, m. p. 167°. It is isomeric and not identical with the dimethylglyoxalines described in the following note. On oxidation, it yields ammonia, methylamine, and acetic acid.

Methylamylglyoxaline, from *iso*pilocarpine, boiled at 158—160° under 10 m.m. pressure; *platinichloride*, m. p. 198°; *picrate*, m. p. 134°; *aurichloride*, amorphous. On oxidation, this base yielded ammonia, methylamine, and *n*-hexoic acid.

Methylamyleneglyoxaline, which probably exists in the fraction boiling at 145—160° under 10 m.m. pressure, was not isolated; its presence was inferred from the formation of butyric acid during oxidation.

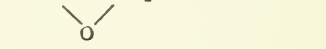
*iso*Pilocarpinolactone, on oxidation with permanganate, yielded ammonia, methylamine, and pilopic acid, whilst pilocarpine gave rise to ammonia, methylamine, and homopilopic acid.

*iso*Pilocarpine, which could not be reduced electrolytically, did not form diacidic salts, and on titration behaved as a normal lactone.

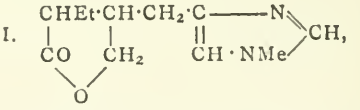
*iso*Pilocarpine methiodide with picric acid, yielded the compound previously described as methyl*iso*pilocarpine picrate, but which should be termed *iso*pilocarpine methyl picrate.

The absorption spectra of pilocarpine and *iso*pilocarpine, kindly determined by Prof. J. J. Dobbie, were absolutely identical.

The following formulæ were proposed for pilocarpine and *iso*pilocarpine:—



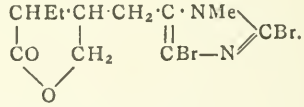
or—



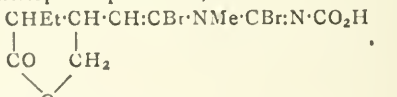
and it was suggested that pilocarpine and *iso*pilocarpine are stereoisomerides, the asymmetric carbon atom involved being that contiguous to the carboxyl residue.

The following configurations were proposed on the basis of formula I.:—

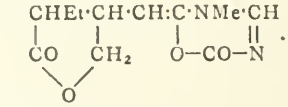
Dibromopilocarpine or dibromo*iso*pilocarpine,—



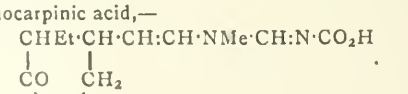
Dibromo*iso*pilocarpinic acid,—



*iso*Pilocarpinolactone,—



*iso*Pilocarpinic acid,—



Bromocarpinic acid,—

It was shown that the explanation given by Pinner and Schwarz of the formation of pilocarpoic acid, $C_{11}H_{16}O_5N_2$, is quite untenable, but no suggestions as to the constitution of this substance or pilomalic acid were offered.

*33. "*Preparation and Properties of* 1 : 4(*or* 1 : 5)-*Dimethylglyoxaline and* 1 : 3-*Dimethylpyrazole.*" By H. A. D. JOWETT and C. E. POTTER.

These bases were prepared in order to compare their reactions with those of *iso*pilocarpine.

1 : 4(or 1 : 5)-*Dimethylglyoxaline*, obtained from 4(or 5-methylglyoxaline (hitherto described as a liquid, but now obtained in crystals, m. p. 55°), is an oil boiling at 203°, and forming an *aurichloride*, m. p. 215°; *platinichloride*, m. p. 239°; *picrate*, m. p. 167°; *methiodide*, m. p. 156°; and *hydrochloride*, m. p. 145°. Bromine gave a crystalline *dibromo*-derivative, m. p. 127°, but at 100° under pressure the reaction was complicated, and a crystalline acid was produced. On oxidation, the base yielded ammonia, methylamine, and acetic acid, whilst by the action of potassium hydroxide the methiodide gave methylamine and acetic acid.

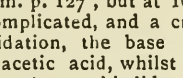
1 : 3-*Dimethylpyrazole*, prepared from 3-methylpyrazole, is a liquid boiling at 148°, which gives an *aurichloride*, m. p. 175°; *platinichloride*, m. p. 234°; *hydrochloride*, m. p. 160°; and *methiodide*, m. p. 256°. Bromine under ordinary conditions, or at 100° under pressure, gave a *dibromo*-derivative, m. p. 74°; 1-*methylpyrazole*-3-*carboxylic acid*, m. p. 222°, was obtained by oxidation of the base. The methiodide was scarcely attacked by potassium hydroxide.

Prof. C. R. Marshall states that these bases have no physiological action analogous to that of pilocarpine.

1 : 2-Dimethylglyoxaline forms a *picrate*, m. p. 179°; an *aurichloride*, m. p. 215°; a *platinichloride*, m. p. 230; and a *methiodide* which does not melt below 300°.

*34. "*Camphor-β-thiol.*" By T. M. LOWRY and G. C. DONINGTON.

Camphor-β-thiol,—



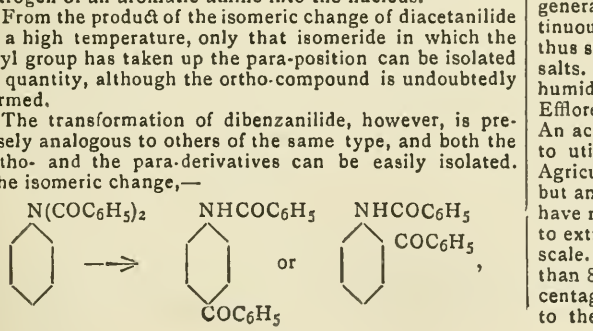
prepared by reducing the sulphochloride of Reychler's camphorsulphonic acid, is a colourless solid, of characteristic and not unpleasant odour, readily volatile with steam, which crystallises from alcohol in small, glistening prisms, and melts at 66°; $[\alpha]_D = +6°$ (in acetone). It is insoluble in alkalis, but forms a lead salt and a mercurichloride, $ClHg{\cdot}S{\cdot}C_{10}H_{15}O$. The disulphide melts at 224°; $[\alpha]_D = -90°$ (in acetone). The acetate, $AcS{\cdot}C_{10}H_{15}O$, forms needle-shaped crystals melting at 38°; $[\alpha]_D$ 8° $= -41°$ (in acetone). The benzoate, $BzS{\cdot}C_{10}H_{15}O$, melts at 59°; $[\alpha]_D$ 13° $= -16°$ (in acetone).

*35. "*Isomeric change of Dibenzanilide into Benzoyl-o-amino- and Benzoyl-p-amino-benzophenones.*" By F. D. CHATTAWAY.

The author has previously shown (*Proc.*, 1902, xviii., 173) that acyl groups must be included among those which, under suitable circumstances, can pass from the nitrogen of an aromatic amine into the nucleus.

From the product of the isomeric change of diacetanilide at a high temperature, only that isomeride in which the acyl group has taken up the para-position can be isolated in quantity, although the ortho-compound is undoubtedly formed.

The transformation of dibenzanilide, however, is precisely analogous to others of the same type, and both the ortho- and the para-derivatives can be easily isolated. The isomeric change,—



which takes place readily under the influence of hydrogen chloride, is best effected by heating aniline (1 mol.) with benzoyl chloride (2 mols.) for eighteen to twenty hours at about 220°.

The product is hydrolysed by alcoholic hydrochloric acid, and the alcohol driven off in a current of steam. On adding water, the bases, which remain in solution as hydrochlorides, can be separated from tarry matters, and any unchanged aniline removed by making the solution alkaline with sodium hydroxide and distilling in steam. On cooling, the other bases solidify, and on dissolving the dry product in a little alcohol and adding a slight excess of strong sulphuric acid, the sparingly soluble sulphate of *p*-aminobenzophenone crystallises out. On making the mother-liquor alkaline and distilling in superheated steam, *o*-aminobenzophenone slowly distils over and crystallises from the distillate in a pure state.

About 45 grms. of *p*-aminobenzophenone and 15 grms. of *o*-aminobenzophenone can be obtained from 100 grms. of aniline.

*36. "*Formation of Purpurogallin by the Electrolytic Oxidation of Pyrogallol.*" By A. G. PERKIN and F. M. PERKIN.

The methods hitherto employed for the production of purpurogallin give only a poor yield, but recent experiments made by the authors on the electrolytic oxidation of pyrogallol have shown that, in general, the quantity of purified product amounts to 37—45 per cent of the calculated amount. The purified substance, which had all the properties of purpurogallin, and its acetyl derivative, gave, on analysis, figures which established its identity with this colouring matter.

The composition of the electrolytic bath has been frequently varied, and recently a solution containing 28 grms. of pyrogallol, 10 c.c. N-sulphuric acid solution, and 50 grms. of sodium sulphate in 500 c.c. of water has been found to be most effective. The best results have been obtained by using a rapidly rotating anode of platinum-iridium and a cathode of lead or graphite. The current density was 4—6 ampères with an E.M.F. of 8—10 volts, The behaviour of other phenolic substances under similar conditions is now under investigation. Gallic acid yields a small quantity of a product which probably contains the purpurogallincarboxylic acid recently described (*Trans.*, 1903, lxxxiii., 199).

37. "*The Analysis of* Reh, *the Alkaline Salts in Indian* usar *Land.*" By E. G. HILL.

The upland barren lands of India, extending over an area of about two million acres, which are mainly found betweed the Jumna and the Ganges, and also between the latter and the Gogra, contain so large a quantity of soluble salts in the soil that agriculture is practically impossible. The reclamation of this land has occupied the attention of the Government of India for many years, but less effort has been made to utilise the soluble salts. Such lands have the following general features :—The soil is impermeable for a varying depth below the first few inches; below the impermeable layer is a coarser layer, more or less porous, in which nodular limestone is generally found, and this is sometimes so thick and continuous as practically to form a rock. The upper soil is thus shallow and fitted for the concentration of soluble salts. Such land varies in appearance according to its humidity and the amount of salts which it contains. Efflorescence is frequent, and a grey colour is general. An account of the various attempts which have been made to utilise *usar* land has been published in the "Indian Agricultural Ledger" (1901, No. 13) by W. H. Moreland, but analyses of the soluble salts contained in these soils have not been recorded, and no attempts have been made to extract these substances and employ them on a large scale. Out of the samples analysed, none contained less than 88 or 89 per cent of sodium carbonate, but the percentage of salt in the soil varies very materially according to the district and the sub-soil. In the districts where

there is a considerable quantity of alkali in the soil, the upper layers are collected and sold under the name of *sujji muttee*. This is used by native washermen in place of soap, and in Allahabad one tradesman makes a crude soap by boiling the solution of this earth with lime and castor oil.

Glass has also been made from this sodium carbonate, the chief product being the glass bangles which are so common in the country; sodium hydroxide has also repaid its manufacture, especially in the vicinity of paper mills. Both sodium carbonate and sodium hydroxide are, however, largely imported into India; the former, especially, being employed in the aëration of mineral waters.

It was thought that *reh* might be interesting from a chemical point of view, and it was examined in order to ascertain whether any sodium sesquicarbonate was present, since this substance occurs in other parts of the world as the native carbonates, *trona* and *urao*.

Each sample of earth was digested with hot water several times, and the solution filtered. In each case, the light brown solution thus obtained yielded on evaporation large and well-defined crystals of the decahydrated normal carbonate, but fractional crystallisation gave a few monoclinic crystals imbedded in the solid mass produced by slowly evaporating the third fraction. These became opaque on being scratched, and were possibly efflorescent.

The solution, which contained a considerable amount of humus, was evaporated to dryness on the water-bath, the residue being freely powdered and dried in a steam oven until the weight was constant. This was a long and tedious process; the weight diminished steadily for forty-eight hours, although less than half a grm. of the substance was taken. There is therefore probably some hydrogen carbonate in the soluble salts. When the weight was constant, a combustion was made with the following result:—

0·3892 grm. gave 0·0278 CO_2 and 0·0078 H_2O with a residue of 0·3584 Na_2CO_3.

The loss in the dried sample was thus 0·0308 grm. or approximately 8 per cent, a result which was confirmed by igniting other portions of the dried salt in a weighed crucible.

Assuming that humus is half the weight of the CO_2 derived from it, and that the difference between the gain in the absorption tubes and loss in the combustion boat is due to oxidation of humus, we get 0·0048 grm. of humus or 0·0096 grm. of CO_2 due to humus. This leaves 0·0182 grm. of CO_2 due to the decomposition of sesquicarbonate at red heat.

The corresponding quantity of sesquicarbonate is 0·1133, which would yield 0·0075 grm. of water. The water found was 0·0078 grm. Hence the dried salt contained 29·9 per cent of sesquicarbonate. The above experiments were made with the Pertabgarh sample.

The soluble salts in five samples from different districts were analysed with the results shown in the Table (Section A.).

There were slight traces of silica and lime in each sample. These analyses indicate that the five samples have the percentage compositions shown in Section B.

	District.				
	Pertabgarh.	Benares.	Mirzapur.	Allahabad, trans-Ganges.	Allahabad, trans-Jumna.
	Percentage of soluble salts.				
	6·3.	3·1.	16·6.	6·3.	6·5.
	A.				
Na_2O ..	57·70	57·72	56·70	57·60	57·61
CO_2 ..	39·72	39·40	36·97	39·17	39·33
Al_2O_3 ..	0·31	0·12	0·12	trace	trace
SO_3 ..	—	—	5·26	2·32	1·71
Cl	2·06	2·67	0·73	0·77	1·06
P_2O_5 ..	0·56	0·45	0·38	0·35	0·64
	100·35	100·36	100·16	100·21	100·37
	B.				
Na_2CO_3 .	95·63	95·08	88·90	94·38	94·80
NaCl ..	3·39	4·40	1·20	1·21	1·75
Na_2SO_4 .	—	—	9·34	4·12	3·02
P_2O_5 } ..	As above.				
Al_2O_3 }					

38. "*Experiments on the Synthesis of Camphoric Acid.* Part III. *Synthesis of* Isolauronolic *Acid.*" By W. H. Perkin, jun., and J. F. Thorpe.

When ethyl cyanodimethylsuccinate,—

$$CO_2Et{\cdot}CMe_2{\cdot}CH(CN)\,CO_2Et,$$

prepared by treating the sodium compound of ethyl cyanoacetate with ethyl bromo*iso*butyrate, is digested with sodium ethoxide and ethyl β-iodopropionate in alcoholic solution, *ethyl cyanodimethylbutanetricarboxylate*,—

$$CO_2Et{\cdot}C(CN)\lessdot\begin{matrix}CH_2{\cdot}CH_2{\cdot}CO_2Et\\ CMe_2\text{——}CO_2Et\end{matrix}'$$

is obtained as an oil which distils at 210—215° under 13 m.m. pressure.

On hydrolysis with dilute sulphuric acid, this ester is converted into *dimethylbutanetricarboxylic acid*,—

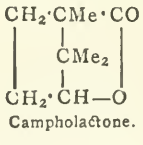
$$CO_2H{\cdot}CH\lessdot\begin{matrix}CH_2{\cdot}CH_2{\cdot}CO_2H\ (a)\\ CMe_2\text{——}CO_2H\ (b)\end{matrix}'$$

a colourless, crystalline substance which melts at 155—157°.

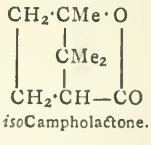
When the trisodium salt of this acid is digested with acetic anhydride, carbon dioxide and water are eliminated between the two carboxyl groups (*a*) and (*b*), and *keto-dimethylpentamethylenecarboxylic acid*,—

$$CO_2H{\cdot}CH\begin{matrix}\diagup CH_2\text{—}CH_2\\ \\ \diagdown CMe_2{\cdot}CO\end{matrix},$$

is formed. This acid crystallises well, melts at 110°, yields an ethyl ester distilling at 172° (100 m.m.), and a semicarbazone melting at 217°. The ethyl ester, when treated with magnesium methyl iodide in ethereal solution, is converted into a lactone which distils at 155—157° (50 m.m.), and has a most penetrating odour of peppermint. This new lactone, for which the name iso*campholo-lactone* is proposed, is isomeric with campholactone, and the close relationship which exists between these two substances is obvious when their formulæ are written side by side:—



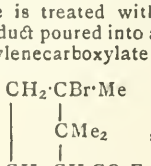
Campholactone.



*iso*Campholactone.

The above formation of *iso*campholactone constitutes the first synthesis of that trimethylpentamethylene ring which is the basis of camphoric acid and of so many other substances belonging to the camphor group, and it is hoped that it may ultimately be possible to obtain camphoric acid itself from this lactone.

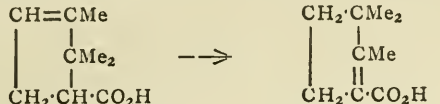
When the lactone is treated with phosphorus pentabromide and the product poured into alcohol, ethyl bromotrimethylpentamethylenecarboxylate is formed:—



and is an oil which distils at 165°—170° under 70 m.m. pressure.

In an experiment in which this bromo-ester was heated with potassium cyanide in alcoholic solution, and then

with alcoholic potash, a quantity of an oily acid was obtained which was obviously inactive α-campholytic acid, produced from the bromo-ester by elimination of hydrogen bromide and subsequent hydrolysis. This was proved by the fact that, on distillation with dilute sulphuric acid, the oil was converted into a crystalline acid melting at 132°, which, on examination, was easily identified as iso*lauronolic acid*, the well-known isomeric change indicated by the formulæ :—



α-Campholytic acid. *iso*Lauronolic acid.

having taken place,

That the *iso*lauronolic acid, thus synthesised, is identical with *iso*lauronolic acid obtained from camphoric acid was shown by mixing equal quantities of the two preparations, when the mixture melted at 132°, the melting-point of the constituents. Furthermore, the synethetical acid, on oxidation with permanganate, yielded *iso*lauronic acid.

(To be continued).

NOTICES OF BOOKS.

Report on the Agricultural Work in the Botanic Gardens and Government Laboratory for the Years 1896-1901, *at Georgetown, Demerara.* By J. B. Harrison, Government Analyst. Printed by the Authority of His Excellency the Governor. Georgetown : C. K. Jardine. 1902. Pp. 136.

The report now before us is somewhat belated, but this is explained by the failing health and subsequent death of Mr. G. S. Jenman, who for some years past has collaborated with Mr. Harrison.

The report has been divided into two parts. Part I. deals with the meteorology of the period under review, with the experiments carried on with varieties of sugar-canes, especially with the production of new varieties from seed, and with the manurial experiments; and Part II., on various other subjects of agricultural interest which have occupied the attention of the two departments during recent years.

Perhaps the most valuable portion of the report is to be found in Chapter IV. on Manurial Experiments. Some of the conclusions arrived at as a result of these experiments are both interesting and valuable, especially as they are formed on experiments lasting over eleven years.

It is found that nitrogen is an essential constituent of sugar-cane manures, as in each crop the manurings with nitrogen gave greatly increased yields, 40 lbs. of nitrogen in the form of either sulphate of ammonia or nitrate of soda having yielded, on the average, 6·9 tons of produce, which could yield 0·56 ton of first and second sugars per acre. In other words, 10 lbs. of nitrogen, on land not limed, is equivalent to 1·6 tons of canes, or nearly 3 cwts. of sugar.

The West Indies and British Guiana have had a hard struggle for many years, but they have tackled the problem of making sugar-growing profitable in a plucky manner, and we trust that now, aided by Legislative measures concerning Sugar Bounties, they are on the eve of another era of prosperity, such as they enjoyed in olden times, before beetroot sugar became so dangerous a competitor.

The Figures, Facts, and Formulæ of Photography, and Guide to their Practical Use. Edited by H. Snowden Ward. London: Dawbarn and Ward, Ltd. 1903. Pp. 166.

This volume will no doubt be of use to photographers, containing as it does a large amount of information in a condensed form. It is divided into thirty-three sections, and there can be no complaint that it does not begin at the beginning.

The first paragraph in Section I., on the Studio, is on how to make fabrics and materials fireproof; the author, however, does not recommend the use of tungstate of soda, a salt we have found to be efficacious. In a subject so wide as photography the difficulty is to keep the volume of facts within reasonable limits; the endeavour here has been to include only all that is necessary for practical working, while there are also a few sections on what may be called allied subjects, such as the law of copyright, toilet and hygiene, poisons and their antidotes, &c.

CORRESPONDENCE.

PATENT LAW IN THE UNITED STATES.

To the Editor of the Chemical News.

Sir.—We have received information of important changes in the United States Patent Law to the effect that the Senate on the 3rd inst. passed a Bill (No. 17085) to give effect to the provisions of the International Convention, the Bill having previously passed the House of Representatives. The Bill was signed by the President on the 4th inst., and now has the force of law.

The Bill provides for giving priority to applications filed under the International Convention, and also provides, in respect to applications filed otherwise than under the Convention, that they shall not be refused by reason of the invention being previously patented abroad, unless the application for the foreign patent was filed more than *twelve* months before the application in this country. The fourth section of the Bill extends the right of filing Caveats to foreigners; so that, as the law now stands, any person, whether a citizen of the united states or foreigner, may file a Caveat. The second section of the Bill amends Section 4892 of Revised Statutes, to the extent that oath may now be taken before any Notary Public, Judge, or Magistrate having Official Seal and authorised to administer Oaths in the foreign country in which the applicant may be. This section of the Bill, however, requires that in case of oath taken before a foreign Notary, Judge, or Magistrate, must be legalised. The third section of the Bill amends Section 4896 of Revised Statutes, so that a foreign-appointed Executor may apply for patent in this country without being required to take out ancillary letters of administration in this country.

The importance of this amendment in the American Patent Law has very far-reaching effects, and will no doubt be of interest to your readers,—We are, &c.,

J. E. Evans-Jackson & Co.

Bristol House,
19 & 20, Holborn Viaduct, London, E.C.,
March 17th, 1903.

The Chemical Laboratory at Wiesbaden.—During the Winter Term, 1902-03, the Chemical Laboratory Fresenius was attended by thirty-seven Students. Of these, twenty-eight were from Germany, two from Russia, one from Austria, one from Switzerland, one from Italy, one from England, one from Sweden, one from Spain, and one from the Transvaal. There were three Assistants in the Instruction Laboratory, and twenty-four in the Versuchsstationen (private laboratories). To the body of teachers belong the Directors, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Prof. Dr. Med. G. Frank, Dr. L. Grünhut, and J. Huber (Architect). The next Summer Term begins on April 24th. During the Winter Term, 1902-03, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen), on behalf of trade, manufacture, mining, agriculture, and hygiene.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

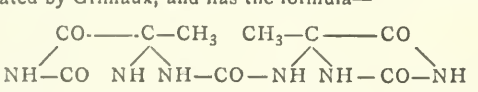
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 8, February 23, 1903.

Law of Electromotive Forces of Saline Solutions. Influence of Temperature.—M. Berthelot.—The relation between the electromotive forces of saline solutions has been previously found by the author. He now further examines the subject to find how the law depends on temperature and concentration. He therefore places the elements of the pile in an Arsonval stove, which can be kept at fixed temperatures, and examines in turn cells containing hydrochloric acid and soda, nitric acid and soda, sulphuric acid and soda, boric acid and soda, acetic acid and soda, and finally formic acid and soda. An absolute relation was not determined between the temperature and the electromotive force.

The Influence of certain Treatments on the Micro-structure of Nickel Steels.—Léon Guillet.—The author examines the micro-structure of nickel steels when subjected to the following treatments:—Tempering, heating, strain, chilling, cementation, and decarburation. His results point to the fact that a micro-examination of the surface of steel is much more sensitive than either mechanical or magnetic tests to the transformations undergone by nickel steels by the various treatments.

Certain Products of the Reduction of Copper Salts by Hydroxylamine.—E. Péchard.—The reduction of copper in ammoniacal solution by hydroxylamine serves as the starting point for the preparation of a number of new cuprous salts, such as cuprous acetate and ammoniacal cuprous sulphate.

Action of Urea on Pyruvic Acid. (II.). Dipyruvic Triuride.—L. J. Simon.—The author examines the action of concentrated hydrochloric acid on homoallantoïne, the second product of the action of urea on pyruvic acid. Dipyruvic triuride is thus obtained, which has already been isolated by Grimaux, and has the formula—



The body thus obtained is white and crystalline in fine needles. It is insoluble in organic solvents, very slightly soluble in water, but soluble in alkalis and concentrated mineral acids. Its composition is represented by the formula $C_9H_{12}N_6O_5.2H_2O$. The author examines the action of heat, hydrochloric acid, water, alkalis, and ammoniacal silver nitrate on this body.

Certain Phosphorus Acids derived from Benzophenone and Methylpropylketone.—C. Marie.—The author examines the acids obtained from the action of H_3PO_2 on benzophenone and methylpropylketone and the oxyphosphinic acids which are formed by their oxidation.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xxvii., No. 18—19.

On Perchloric and Periodic Acids.—A. Astruc and H. Murco.—Already inserted in full.

The Complex Salts of Platinum. Reactions of the Plato-oxalonitrites.—M. Vèzes.—Already inserted in full.

Two New Sugars obtained from Manna, Manneotetrose, and Manninotriose. The Composition of Manna.—C. Tanret.—Manna, used by pharmaceutical chemists, is a sugary exudation from the ash-tree, *Fraxinus ornas* and *F. rotundifolia*, cultivated in Southern Europe. The author describes the method used for the extraction of the two sugars, manneotetrose and manninotriose, as well as their composition, properties, and general characteristics. Anhydrous manneotetrose has the formula $C_{24}H_{42}O_{21}$, it crystallises in water with $4{\cdot}5H_2O$, and in alcohol at 90° with $4H_2O$. The hydrolysis of manneotetrose by means of dilute mineral acids shows it to be a tetrose; 1 molecule of manneotetrose is transformed by the fixation of water into 4 molecules of monoses; that is, 2 of galactose, 1 of glucose, and 1 of levulose, according to the equation $C_{24}H_{42}O_{21} + 3H_2O = 4(C_6H_{12}O_6)$. Manninotriose has the formula $C_{18}H_{32}O_{16}$. When hydrolysed by dilute mineral acids it splits up into 2 molecules of galactose and 1 of glucose, and is thus undoubtedly a triose. The author found two samples of manna to have the following compositions:—

	Per cent.	Per cent.
Mannite	40	55
Water	10	10
Glucose	3·0	2·2
Levulose	3·4	2·5
Manneotetrose ..	16·0	12·0
Manninotriose ..	16·0	6·0
Salts	2·0	1·5
Resin	0·1	0·05
Undetermined ..	the remainder	

The Solubility of Prussian Blue.—G. Wyrouboff.—A criticism of M. Coffignier's paper on the same subject in the *Bull. Soc. Chim.*, Series 3, vol. xxvii., p. 696.

The Double Nitrites of Iridium.—E. Leidié.—Already noticed.

New Method for the Purification of Potable Waters.—P. Guichard.—Already inserted.

A New Di-iodised Phenol.—P. Brenans.—Already noticed.

Some Organic Compounds of Addition.—M. Lemoult.—The author finds that the polynitrated benzenic derivatives having 1 atom of chlorine, or an HO group, or an NH_2 group, unite with the greatest facility with the substituted *p*-diamised derivatives of diphenylmethane, giving well crystallised compounds of addition, resulting from the juxtaposition of the 2 molecules used, and easily decomposed into their constituents.

Some Derivatives of β-Naphthylamine.—A. Reychler.—The author gives some details concerning the preparation and properties of methylethyl-β-naphthylamine. When we enclose in a sealed tube an equimolecular mixture of ethyl-β-naphthylamine and iodide of methyl and a small quantity of methylic alcohol, we observe that a reaction commences immediately with a marked rise of temperature. After heating to 100° for a quarter of an hour the contents of the tube are cooled, poured into water, and decomposed by the addition of caustic soda; this gives a mixture of insoluble products, which may be collected in a supernatant layer of benzene. The aqueous layer contains not only an alkaline iodide and some soda, but a considerable amount of a quaternary iodide of ammonium, which separates in the cold in the form of an oily deposit, and even crystallises eventually. The benzenic layer is purified by several washings with warm water; it contains methylethyl-β-naphthylamine and unchanged ethyl-β-naphthylamine, which are separated by drying and concentrating the benzenic solution and heating the residue with an excess of acetic anhydride. After heating for an hour to about 90° or 100°, the whole is poured into dilute hydrochloric acid, and two solutions are obtained; (1) a benzenic solution of acetylised ethylnaphthylamine, and (2) an acid aqueous solution of methylethylnaphthylamine.

The Analysis of Lithopone.—Ch. Coffignier.—Already inserted.

The Stereo-chemistry of Nitrogen.—A. Reychler.—Not suitable for abstraction.

The Stereo-chemistry of Nitrogen and the Rotatory Power of *d*-Camphorsulphonate of Methylethyl-β-naphthylamine.—A. Reychler.—I. Solutions were made in a mixture of about 9 parts of acetic ether and 1 part of absolute alcohol. The temperature of the determinations (*d* and α) was 20°. Concentration of the solutions, *p* = 7 to 8 per cent.

d-Camphorsulphonate of dimethyl-β-naphthylamine $[\alpha]_D$	= +35°
d-Camphorsulphonate of methylethyl-β-naphthylamine—First fraction	+32°
Second fraction.. ..	+32·1°
d-Camphorsulphonate of diethyl-β-naphthylamine	+27°

II. Alcoholic solutions. Temperature = 20, *p* = about 7 per cent.

d-Camphorsulphonate of dimethyl-β-naphthylamine $[\alpha]_D$	= +30°
d-Camphorsulphonate of methyethyl-β-naphthylamine — First and second fractions	+28°
d-Camphorsulphonate of diethyl-β-naphthylamine	+26·5°

Action of Tetrazoic Chlorides on Oxalacetate of Ethyl.—J. Rabischong.—A tenth of a molecule or 18·4 grms. of benzidine is dissolved in 50 c.c. of hot hydrochloric acid at 40 per cent and 250 c.c. of water. The solution, cooled down to 0° with ice, is treated with a solution of nitrite of soda at 13·8 per cent. The tetrazoic chloride obtained is then treated with 90 grms. of acetate of soda dissolved in 200 c.c. of water. The filtered solution is poured gradually into 37·6 grms. of oxalacetic ether dissolved in 300 c.c. of alcohol kept at 0°. Immediately a deep red mass separates, which, after washing and drying, is easily soluble in xylol. Supersaturated hot solutions deposit small carmine-red crystals on cooling; they consist of diphenyldihydrazone-oxalacetate of ethyl. The author describes several other bodies obtained in a similar manner.

The Rotatory Power of Hydrochlorate of Cocain.—M. Imbert.—The rotatory power of hydrochlorate of cocain in water and alcohol at 40° diminishes as the concentration is augmented. It becomes constant at −67° 50′, in alcohols at 65° to 80°. The constant value $[\alpha]_D$ is exactly that given by a 10 per cent aqueous solution and a solution of alcohol at 40° containing 6 per cent of salt.

Essence of Badiane from Japan.—E. Tardy.—By fractional distillation, which, however, does not give very satisfactory results, two groups of substances are obtained, one from 150° to 180°, and the other from 220° to 280°; the author describes various experiments and treatments of these two portions.

Essence of Badiane from China.—E. Tardy.—This essence is very different from the Japanese essence, and can be divided by fractional distillation into many more portions, at least two dozen, from that coming over below 150° to that coming over at 230—235°. It contains pinene, phellandrene, estragol, dextrogyre terpilenol, anethol, a levogyre sesquiterpene, anisic aldehyd, anisic acetone, anisic acid, a small quantity of a crystallised body with the formula $C_{20}H_{22}O_3$, and an equally small quantity of ethylic ether of hydroquinone.

Essence of Bitter Fennel.—E. Tardy.—The author gives the analysis and properties of essence of bitter fennel from Algiers and one from Galicia. The quantities of hydrococarbons and that of estragol are greater in the Algerian essence than in that from Galicia. It is the effect of the influence of climate.

Examination of "Civet."—A. Hébert.—Besides the specific differences found to exist in the secretions from different individuals, the author finds that in commercial samples the composition of "civet" is further influenced by the method of extraction adopted.

The Estimation of Alcohol in very Dilute Solutions.—G. Argenson.—Already inserted in full.

Action of Blood on Peroxide of Hydrogen.—J. Ville and J. Moitessier.—Blood decomposes peroxide of hydrogen with an energy which varies according to the species of the animal used, but it is indispensable to take note of the acidity of the peroxide used, or the results will vary considerably. The authors have also examined the effect of the influence of the quantity of peroxide used; that of the dilution of the blood, and the dilution of the peroxide, and they find that the acidity and the dilution of the peroxide have the greatest effect on its action.

MISCELLANEOUS.

Photographic.—Messrs. Welcome and Co. have published a small Exposure Record and Diary, in pocket-book form, full of information useful to the photographer. The Diary, printed on tough thin paper, includes a light table for each month; and there is an ingenious exposure calculator at the end of the book.

Institute of Chemistry of Great Britain and Ireland.—The next Examinations of the Institute of Chemistry, for persons desirous of qualifying themselves to be public and technical analysts, will be held in July, 1903. The Examinations are open only to candidates who have complied with the Regulations. The Intermediate Examination will be held at 30, Bloomsbury Square, London, W.C., and at the Glasgow and West of Scotland Technical College, George Street, Glasgow, commencing on Tuesday, July 7th. Examinations in the following branches of the Final Examination for the Associateship (A.I.C.) will be held in London, and may commence on either July 7th or 14th :—(*a*) Mineral Chemistry, (*b*) Metallurgical Chemistry, (*c*) Physical Chemistry, (*d*) Organic Chemistry, and (*e*) The Analysis of Food and Drugs, and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy. The Final Examination in the branch of Biological Chemistry will be held in October.

The Solution of Molecular Combinations.—G. Bodlaender and R. Fittig.—The solubility of an insoluble salt in the solution of a body capable of forming a molecular combination with it, does not give any precise indications. Thus it is that the study of the solutions of chloride of silver in ammonia gives results which only agree very indifferently with the formulæ, $AgCl(NH_3)_2$, $(AgCl)_2(NH_3)_3$, $(AgCl)_3(NH_3)_4$, and $(AgCl)_m(NH_3)_{m+1}$. To recognise the value of *m*, it is necessary to examine the solubility of AgCl in solutions containing, besides ammonia, chlorides or nitrate of silver. In both cases the solubility of the AgCl is diminished; its variation with the contents of the solution in chlorine or in silver gives for the dissolved complex salt the formula $AgCl(NH_3)_2$. Bromide of silver gives a compound with a similar formula. Both chloride and bromide of silver are insoluble in solutions containing only 2 molecules of NH_3 per molecule of AgCl or AgBr; an excess of ammonia is necessary to prevent the dissociation of the complex ion. On the other hand, the soluble salts of silver only require an amount of NH_3 hardly greater than 2 molecules, in order to give the complex salt. The constant of dissociation of the complex ion, $Ag(NH_3)_2$, into Ag and $2NH_3$ can be deduced, not only from the measurements of solubility, but also from the measurements of the electromotive force; its value is :— $k = \frac{Ag + 2NH_3}{Ag(NH_3)_2} = 6{\cdot}8 \,.\, 10^{-8}$. The free energy corresponding to this transformation into normal solution is 9832 calories.—*Zeit. Physik. Ch.*, vol. xxxix., p. 597.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Society of Arts, 8. (Cantor Lectures). "Hertzian Wave Telegraphy in Theory and Practice," by Prof. J. A. Fleming, M.A., D.Sc., F.R.S.

TUESDAY, 24th.—Royal Institution, 5. "Great Problems in Astronomy," by Sir Robert Ball, F.R.S.

WEDNESDAY, 25th.—Society of Arts, 8. "Oil Light by Incandescence," by Arthur Kitson.

THURSDAY, 26th.—Royal Institution, 5. "Society during the Commonwealth and Protectorate," by Charles Harding Firth, M.A.

FRIDAY, 27th.—Royal Institution, 9. "The Pearl Fisheries of Ceylon," by Prof. W. A. Herdman, D.Sc., F R S.

SATURDAY, 28th.—Royal Institution, 3. "Light—its Origin and Nature," by Lord Rayleigh, F.R.S., &c.

CITY OF BIRMINGHAM.

MUNICIPAL TECHNICAL SCHOOL.

The Corporation require, in September next, the services of a HEAD of the CHEMISTRY DEPARTMENT, which post will be then vacant owing to the retirement of Mr C. J. Woodward under the Superannuation Scheme. The commencing salary offered is £300 per annum.

The last date for sending in applications is APRIL 8th.

Personal convassing of members of the Committee by applicants or their friends will be a disqualification.

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GEO. MELLOR, Secretary.

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LECTURES.

Experimental Chemistry (Inorganic) — Prof. H. FRESENIUS, Ph.D.
Experimental Physics .. .. — Prof. W. FRESENIUS, Ph.D.
Stöchiometry .. ..
Organic Chemistry .. .. — L. GRÜNHUT, Ph.D.
Chemical Technology .. ..
Microscopy, with exercises in Microscopic work .. .. — W. LENZ, Ph.D.
Chemistry and Analysis of Foods .. — Prof. H. FRESENIUS, Ph.D., Prof. W. FRESENIUS, Ph.D., and Prof. E. HINTZ, Ph.D.
Hygiene .. .. — Prof. Dr. med. G. FRANK.
Practical exercises in Bacteriology .. — J. HUBER.
Technical Drawing, with exercises ..

The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to one of the Directors.

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Re Pirie *v.* The Electro-Chemical Co. (1900), Ltd., 1901, E. 85.—By order of Mr. Justice Farwell.—Mr. F. J. Terry Horsey, of the firm of—

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comprises seven Lead Bleach Chambers, two measuring 100 feet by 26 ft. each, and five 80 ft. by 25 ft.; four cast-iron Absorbers; twelve 12- and 16-ton Caustic Soda Pots; seventeen steel Evaporating and Crystallising Tanks; 200 slate Decomposing Tanks with cells and copper connections, mixers, and sifters; six Steam Pumps; Blowing Engine; and quantity steel and iron Tanks and Receivers; and in addition there is a nearly new 10-in. saddle-tank Loco, 20-ton Weighbridge, two Overhead Travellers, ten Auxiliary Steam-engines, &c.

Tenders are to be sent in a sealed cover, addressed to Mr. F. J. Terry Horsey, of the firm of Fuller, Horsey, Sons, and Cassell, 11, Billiter Square, E.C., on or before March 25, 1903.

Particulars, with Plan and Conditions of Sale, and Form of Tender, may be obtained gratis of Messrs. Walter Webb and Co., Solicitors, 23, Queen Victoria Street, E.C.; of the Receiver, Robert Shaw, Esq., 50, Denton's Green Lane, St. Helens, Lancashire; and of Messrs. Fuller, Horsey, Sons, and Cassell, 11, Billiter Square, E.C.

ST. PAUL'S SCHOOL, West Kensington.—An EXAMINATION will be held at the above School on Tuesday, April 21st, 1903, and the following days, for filling up Five or more Vacancies on the Foundation.—Full particulars can be obtained on application to the Bursar.

THE CHEMICAL NEWS.

VOL. LXXXVII., No. 2261.

THE POSITION OF RADIUM IN THE PERIODIC SYSTEM AS INDICATED BY ITS SPECTRUM.

By C. RUNGE and J. PRECHT.

THE spark spectrum of radium may be readily observed by using the radium bromide recently prepared by Prof. Giesel. A few milligrms., which Prof. Giesel kindly placed at our disposal for this purpose, were sufficient to enable us to obtain with smaller dispersion a more complete spectrum than had as yet been observed, and with greater dispersion to investigate with regard to their behaviour in the magnetic field the lines which may be easily photographed. We have thus found that the strongest radium lines are completely analogous to the strongest barium lines and to the corresponding lines of the allied elements Mg, Ca, Sr. These may be grouped, as Runge and Paschen have shown (*Ber. d. Berl. Akademie*, June 26, 1902), as three pairs of lines, which, on account of certain analogies with the spectra of the alkalis, they denote as the pair of lines of the principal series, and the pairs of lines of the first and second secondary series. With the pair of lines of the first secondary series close to the line of greater wave-length a fainter line, which Runge and Paschen call a satellite, appears on the side of the greater wave-lengths. Measured on the scale of the oscillation numbers both lines of each of these three pairs have the same distance for each element, only in the pair of the first secondary series instead of the one line the satellite must be taken. For different elements the distance, on the other hand, is different, and it increases with increasing atomic weight in a perfectly uniform manner, as will be further discussed below. In the magnetic field, as Runge and Paschen have shown, these lines split up in various ways into components, in such a manner, however, that, measured on the scale of the oscillation numbers, the splitting up of each line of one element is exactly the same as that of the corresponding line of each of the other elements.

We have now found that the same holds good for radium, so that radium must be placed in a group of chemically allied elements with Mg, Ca, Sr, Ba, as its chemical behaviour (so far as it is known at present) also demands.

In the following table the lines which correspond to one another are placed together:—

	Mg.	Ca.	Sr.	Ba.	Ra.
Principal series ..	2803	3969	4216	4934	4682
	2796	3934	4078	4554	3815
1. Secondary series	—	3181	3475	4166	4436
	2798	3179	3465	4131	4341
	2791	3159	3381	3892	3650
2. Secondary series	2937	3737	4306	4900	5814
	2929	3706	4162	4525	4533

The splitting up of the radium lines in the magnetic field may be very readily observed in the strongest lines. Up to the present we have succeeded in splitting up all the lines except the satellite and the line 5814 in the yellow.

The differences between the two lines of the pairs are, as was mentioned above, the same for each element, when measured on the scale of the oscillation numbers. The same holds good for radium, as the following table shows:—

	λ.	10⁸/λ.	Difference.
Principal series ..	4682·35	21356·8	4858·3
	3814·59	26215·1	
1. Secondary series ..	4436·45	22540·5	4858 5
	3649·77	27399·0	
2. Secondary series ..	5813·9	17200 2	4858·6
	4533·33	22058 8	

The variations of the three differences from one another are adequately explained by errors of observation. They correspond to very small errors in the wave-length determinations.

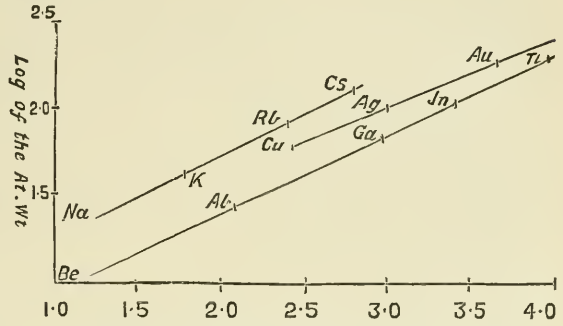


FIG. 1.—Log. of the difference of lines (0·01 scale divisions = 2·3 per cent of the value).

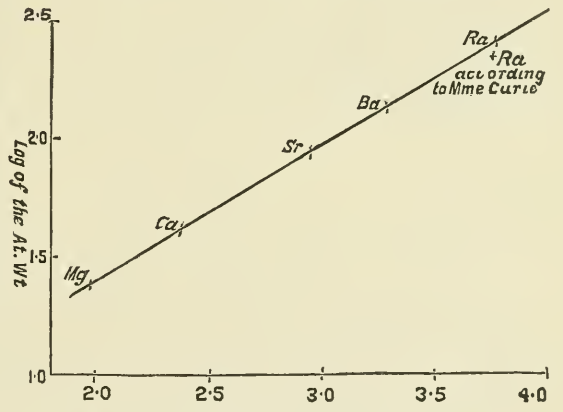


FIG. 2.—Log. of the difference of lines (0·01 scale divisions = 2·3 per cent).

In the case of Mg, Ca, Sr, Ba the differences increase with the atomic weight of the elements.

	Atomic weight.	Difference.
Mg	24·36	91·7
Ca	40·1	223
Sr	87·6	801
Ba	137·4	1691

Hence the atomic weight may be regarded as a function of the difference, and this function may be obtained for radium by extrapolation. In the reports of their researches on the spectra of the elements, Rydberg and Kayser and Runge have already alluded to the fact that the differences of the pairs of lines in a group of chemically allied elements increase regularly with the atomic weight. In the case of the alkalis they state that the atomic weight is very nearly proportional to the square root of the difference. We might mention in regard to this that for the other groups in which pairs of lines have been observed, the relation between the difference of the pairs of lines and the atomic weight may be simply expressed:—

In every group of chemically allied elements the atomic weight is proportional to a power of the difference of the two lines of the pair of lines.

The exponent is a proper fraction. Or otherwise expressed:—

If the logarithms of the atomic weight and difference are taken as co-ordinates, the points corresponding to a group of chemically allied elements lie on a straight line.

In the two accompanying figures this law is illustrated.

In Fig. 1 we see that in the case of the alkalis, only potassium lies somewhat beneath the straight line passing through the other points. We do not wish to say that therefore the atomic weight of potassium as obtained by stochiometric methods is incorrect, but it appears to us interesting that the deviation from the law of the straight line is greater in the case of the identical element whose atomic weight in the periodic system points to some unknown disturbing circumstance, causing the inverted position of argon and potassium.

As regards boron, gallium, and indium, the radiation in the magnetic field in these elements has not been investigated. Nevertheless, there can be no doubt about the pairs of lines, which correspond to those of aluminium and thallium. The same holds good for the alkali group in which only the two yellow sodium lines have been investigated in the magnetic field.

In Fig. 2 the same relation is shown for Mg, Ca, Sr, Ba, Ra. Extrapolation gives the value 258 for the atomic weight of radium. Naturally the straight line may be somewhat turned or moved out of its place without deviating too far from the points, but the figure shows clearly that the value 225 obtained by Mdme. Curie is at some distance from the straight line.

In the following table the straight line is replaced by a formula, and extrapolation by calculation.

If x denotes the difference of the pair of lines, measured on the scale of the oscillation numbers $10/^{8}\lambda$, then we have:—

$$\text{At. wt.} = \text{num. log}\,(0{\cdot}2005 + 0{\cdot}5997 \log x).$$

	Formula.	Observed at. wt.
Mg..	23 84	24·36
Ca..	40 6	40·1
Sr	87·5	87·6
Ba..	136·9	137·4

Extrapolation gives for radium the calculated atomic weight of radium 257·8.

We do not venture to assert that our number is more accurate than the value obtained by Mdme. Curie. Nevertheless, it may be mentioned that owing to the close relationship between barium and radium, and owing to the small quantities of the substance with which the chemist is forced to work, the complete separation of these two substances is very difficult, and Mdme. Curie must have found too low an atomic weight in consequence of incomplete separation. According to the crystallographic observations of F. Rinne, which will shortly be made public, radium bromide and barium bromide are isomorphous with one another, so that a simultaneous crystallisation of the two substances (isomorphous mixture) is *à priori* very probable, supposing that the solubility ratios are similar. Hence the great difficulty in separating the two substances from one another by crystallisation, so that even after constantly repeated crystallisation more or less barium may still be present in the corresponding radium compound. The same holds good for the relation of radium to calcium, as well as to strontium and magnesium.

The number 225 agrees better with the periodic system, inasmuch as it fits into the gap between bismuth and thorium in the right column. If the atomic weight is 258, radium must move two series further in the column Mg, Ca, Sr, Ba, and a number of new unoccupied places arise in the periodic system.

On the other hand, we may bring forward in favour of the greater atomic weight what Rutherford has observed. The greater atomic weight suggests a complicated structure of the atom, and hence a greater tendency for the formation of electrons. The element which forms electrons most readily should thus have also the greatest atomic weight.

The radium line, 4826·14, which appears in the Bunsen flame more distinctly than all the other lines, is also, after being split up in the magnetic field, analogous to the strongest Bunsen flame lines: Ba, 5535; Sr, 4607; Ca, 4226. All these lines may be split up into three components, which in all these elements, when measured on the scale of the oscillation numbers, are at equal distances from one another.—*Physikal. Zeit.*, iv., 285.

A NEW REACTION FOR THE FATTY ACIDS.

By Dr. HANS KREIS.

Bellier proposed the following reaction for the detection of olive oil:—Mix and shake up the oil with an equal volume of a saturated solution of resorcin in benzol and the same amount of nitric acid (density = 1·38) free from nitrous acid.

If the olive oil is pure no colouration is produced, or at most a very slight change is observed; with oils of sesame, arachis, cotton-seed, poppies, nuts, linseed, almond and peach kernels, and castor-oil, an intense though fugitive violet colour is formed. Attempts to replace resorcin by other phenols have not given satisfactory results up to the present.

Phloroglucin, which carries three hydroxylised groups, of which two are in the meta position, like resorcin, appears, however, *à priori*, to be able to possess the same property.

Still, if we operate with a cold benzolic solution of this triphenol, the results are negative on account of its slight solubility under these conditions.

On the other hand, its use either in the solid state or in ethereal solution, or hot benzolic solutions, gives rise to coloured reactions with the fatty acids. The best reactions are obtained with ethereal solutions at 1 per cent. If we place equal volumes of nitric acid, of density = 1·4, the oil to be examined, and the ethereal solution of phloroglucin, and then shake carefully, we notice with oils of arachis, sesame, cotton-seeds, nuts, peach kernels, and castor-oil, that the ethereal solution of the oil, which floats on the top, takes a magnificent raspberry-red colouration. Under these same conditions olive oil and lard and butter oils do not give any colouration, or at the most a pale reddish-yellow tint.

We can detect the same reaction by adding to the oil a little solid phloroglucin, then nitric acid of 1·4 density, and shaking the mixture.

Whenever we use this plan with oil of sesame, that is to say, if we place 0·05 grm. of phloroglucin in a test-tube, moisten it with 3 to 5 drops of the oil and shake up, after adding the same quantity of nitric acid, density = 1·4, we observe that the acid layer takes an intense greenish-blue colour, and the oil turns red. If at this moment we add ether, the latter becomes violet, then on shaking with a little water the last-named takes a deep blue colour, while the ethereal layer becomes reddish-brown.

Further, we can separate in the following manner the blue colouring principle, which is soluble in water:—Dilute the oil of sesame with four parts of tetrachloride of carbon; add to 2 c.c. of this solution about 0·01 grm. of phloroglucin and 1 c.c. of nitric acid of 1·4 density, then shake energetically. A greenish-blue colour is produced, of which the principle can be removed by shaking up with water, which takes an indigo-blue colour. We may mention also that resorcin, either in the solid state or in solution in chloroform, in the presence of oil of sesame,

gives analogous colourations, which disappear rapidly on the addition of ether and water.

In certain cases Bellier's reaction cannot be depended on, especially in the presence of old oils, which only give negative or very indistinct results. On the other hand, if these old oils are mixed with fresh oil of sesame, and hydrochloric acid of 1·19 density is added, a green colouration is formed, as described by Bishop for old oil of sesame. This action has been confirmed by the author for oils of arachis, poppy-seeds, nuts, peach kernels, cotton-seeds, and sesame. Phloroglucin behaves with old oils in the same manner as resorcin.

It results that Bellier's reaction, which is so valuable for the testing of olive oil, since it is the only coloured reaction of oil of arachis that we are aware of, is not absolutely conclusive when it is negative, as fraudulent makers might have recourse to oils not giving this reaction. In such a case, before giving a definite opinion, the olive oil must be shaken up with fresh oil of sesame and hydrochloric acid of 1·19 density, as indicated above, to make sure whether there is any production of the green colour or not.—*Revue International des Falsifications*, January-February, 1903.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 28TH, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, March 10th, 1903.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 196 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Feb. 1st to Feb. 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 196 samples examined by us during the month, 194 were found to be clear, bright, and well filtered; one sample was clear, but dull, and one slightly turbid; this was due to a burst main, and had nothing to do with the filtration, which has been maintained at its usual high efficiency.

The rainfall at Oxford during February has been very low, only 0·01 inch of rain fell before the 21st of the month. The total rainfall was 0·79 inch, the average is 1·80 inches, leaving a deficit of 0·01 inch; this extinguishes the previous excess, and makes a deficit for the first two months of the year of 0·51 inch, or 13·1 per cent on the thirty-five years' average.

The colour of the water has improved, and so has the dissolved organic matter, chiefly of vegetable origin, although the latter is in excess of what it was during the corresponding month last year.

Our bacteriological examinations of 352 samples have given the results recorded in the following table; besides these samples we have examined 198 others from special wells, standpipes, &c., making a total of 550 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	455
New River, filtered (mean of 71 samples) ..	8
Thames, unfiltered (mean of 24 samples) ..	15653
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 185 samples)	23
Ditto ditto .. .. highest	245
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 24 samples) ..	254
River Lea, from the East London Company's clear-water wells (mean of 24 samples) ..	10

Of the 280 daily samples taken from the filter-wells of the Metropolitan Water Companies, and examined bacteriologically by us, eleven samples, or 4 per cent, were sterile; nine samples, or 3·2 per cent, contained more than 100 microbes per c.c.; and two of these samples contained more than 150 microbes per c.c. The mean number of microbes in the 3·2 per cent of samples containing more than 100 microbes was 144, against a corresponding mean of 198 in the 15·1 per cent of samples that contained more than 100 microbes during January. Thus the general microbic condition of the London supply has improved very considerably during the month of February.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE LECITHANS: THEIR FUNCTION IN THE LIFE OF THE CELL.*

By WALDEMAR KOCH.

THE ash left on the incineration of tissues obtained from various parts of the body, especially the brain, has long been known to contain phosphorus. Of the chemical combination in which this phosphorus was present in the original tissues nothing was known until Gobley (*Journ. de Pharm. et de Chim.*, 1850, vol. xvii., p. 401; and vol. xviii., p. 107) carefully studied an organic phosphorus-containing body, which he isolated from eggs and called lecithin. He obtained as splitting products glycerophosphoric acid and some of the fatty acids. Diaconow (Hoppe Seyler's "Medicinisch-chemische Untersuchungen," 1866, vol. ii., p. 221; also *Centralblatt für die Medicinischen Wissenschaften*, 1868, vol. vi., pp. 2, 97, and 434) continued this work at the suggestion of Hoppe Seyler, and isolated as splitting products glycerophosphoric acid, stearic and oleic acids, and a base which he identified with Baeyer's neurin and the neurin obtained by Liebreich (*Liebig's Ann. Chem.*, 1865, vol. cxxxiv., p. 34) from his protagon by decomposition with barium hydrate. From the ease with which his lecitin could be split up Diaconow concluded that it was a neurin salt of distearyl glycerophosphoric acid. This view was, however, disproved by Hundeshagen (*Journ. Prakt. Chem.*, 1883, vol. xxviii., p. 219) on account of the fact that the body prepared by the union of neurin and distearyl glycerophosphoric acid in alcohol solution would not give the characteristic myelin forms, although it possessed all the other properties of lecithin. Strecker (*Liebig's Ann. Chem.*, 1868, cxlviii., p. 78) brought confusion into this subject by identifying the base obtained by him from lecithin with the cholin he had isolated from bile (*Liebig's Ann. Chem.*, 1862, vol. cxxiii., p. 353). Thudichum ("Die Chemische Konstitution des Gehirns des Menschen

* From the *Decennial Publications of the University of Chicago*, 1902, vol. x.

und der Tiere," 1901, p. 123) pointed out the difference between the body derived from bile and the base isolated from lecithin, and identified the latter as neurin by a number of analyses made with carefully purified material. In the book above referred to Thudichum also records some other important observations. Among the large number of compounds isolated by him from the brain there are some which do not contain glycerin; as he always finds phosphorus in the form of orthophosphoric acid, he concludes to call these bodies "phosphatids" and consider them rather as derivatives of orthophosphoric acid than glycerophosphoric acid, as previously accepted. His formulæ resemble the types of the *Typentheorie* of Gerhardt and Wurtz, in leaving the exact building up of the molecule a matter of doubt. From a study of the fatty acids in his various compounds Thudichum concludes, contrary to Diaconow, that there are no phosphatids with only one fatty acid, but that each one contains either palmitic, stearic, or margaric as one of the constituents; which, however, gives no character to the molecule, while the other acid—oleic for brain lecithin, kephalinic for kephalin—gives to the molecule its distinctive properties.

Without considering further the important question of the structure of these compounds, I would propose to classify them under the general term "lecithans." The introduction of the word "lecithan" as a group name seems perferable to the use of an entirely new and unfamiliar term like "phosphatids," as proposed by Thudichum. At the same time, the change of the last syllable of lecithin to *an* gives sufficient variation to prevent any such confusion as attended the generalisation of the word "albumen." The lecithans, then, are substances containing in the molecule phosphoric acid, fatty acids, nitrogen, and, in most cases, glycerin. They resemble each other very closely in their physical appearance, being waxy, non-crystalline, and very hygroscopic. Toward water they all show the same behaviour, although their solubility or the solubility of their salts in *organic* solvents may vary.

The very general distribution of the lecithans in all forms of living tissues speaks for their value in the life of the cell. A more careful study of these compounds indicates that they are valuable in two ways:—First, on account of their physical properties; and, secondly, on account of their chemical behaviour.

Physical Properties.

The behaviour of the lecithans with water seems of especial interest, and can be watched under the microscope. A waxy piece of brain lecithin placed in water first swells up, and then gives off long filaments (called myelins) which sometimes resemble a shepherd's crook, at other times a mass of twisted skein. If allowed to stand for some time, with frequent shaking, a perfect emulsion is finally formed. A lecithan which has been part of the living tissues, such as brain lecithin, gives a much more perfect emulsion than egg lecithin, which is merely stored food material. If such an emulsion is the substratum of the living cell—and there seems good reason to consider it so—it may explain some of the physical properties of living protoplasm. The study of this emulsion is especially interesting in connection with the changes in the physical conditions of the living cell brought about by electrolytes, as shown by the recent work of J. Loeb and his school.

Action of Electrolytes on an Emulsion of Brain Lecithin.—Four g. of brain lecithin (free from calcium, and containing less than 1 per cent sodium or potassium) are treated with one litre of distilled water. The resulting emulsion is sufficiently transparent for purposes of study, can be filtered unchanged, has a neutral reaction to litmus, and remains unaltered for weeks, especially after sterilisation by boiling. The results of my experiments with this emulsion may be classified as follows:—

Univalent Kations.—Salts of Na, K, NH_4, Li, Ag, even in very concentrated solution, give no precipitate, and have apparently no effect on the emulsion. The hydrogen ion is an exception, in the case of acids which are sufficiently dissociated. A concentration of *m*/200 sulphuric will give a precipitate. Carbonic acid is not sufficiently soluble to give any precipitate.

Divalent Kations.—Mg, Ca, Sr, Ba, Co, Ni, Fe", Zn, Cd, Cu, and Pb all give a precipitate which, similar to the one with acids, is flocculent, gelatinous, and settles to the bottom in less than one hour, leaving the supernatant liquid perfectly clear. The concentrations which will just give the precipitate vary somewhat, and have been found in the case of Ca, Sr, and Ba to be *m*/100, *m*/40, and *m*/30, respectively.

Trivalent Kations.—Fe‴, Al, Au give no precipitate, and behave like monovalent kations. Cr gives unsatisfactory results. Au, after standing for several hours, is precipitated in the metallic state.

Anions.—Cl, Br, I, SO_4", *oxalate*, *citrate*, and *ferrocyanide*, $K_4Fe(CN)_6$, give no precipitate, and even in concentrated solution have no apparent effect on the emulsion. OH is an exception, causing the emulsion to clear up.

Non-electrolytes.—Albumins, peptones, glucose, urea, alkaloids, and narcotics like urethan and chloral, give no precipitation reactions and leave the emulsion apparently unchanged. Chloroform has a tendency to be emulsified by the emulsion, a reaction which Thudichum had already observed with ether.

The precipitations above observed with the hydrogen ion and divalent kations seem to be of an entirely physical nature because:—

1. They are independent of the concentration of the lecithin. An *m*/2000 lecithin emulsion will begin to precipitate with about the same concentration of the divalent kation as an *m*/200 emulsion. Stronger emulsions are not sufficiently transparent for observation.

2. Removal of the supernatant liquid by decantation and the addition of water will cause the precipitates to redissolve.

Cadmium, copper, and other salts of various lecithans have been prepared in alcohol solution and analysed, but they are readily broken up on the addition of water, and belong to a class of physical compounds even more unstable than ordinary double salts. It would seem, then, that when a certain limiting concentration of the divalent kation is reached, the emulsion can no longer exist, and the lecithin is precipitated, carrying with it possibly some of the salt. Very interesting, on account of the possibility of furnishing an explanation of such results as Loeb (*Amer. Journ. Phys.*, 1902, vol. vi., p. 411) obtains with Fundulus, are the antagonistic effects of univalent kations in preventing the precipitation. Near the limits at which Ca will just give a precipitate, a very small amount of Na will suffice to prevent this precipitate; as more Ca is added, relatively more Na is needed. A direct comparison of my results with J. Loeb's is not possible, because, in the first place, the amounts of Ca, Na, and lecithin in the Fundulus egg are not known, and, in the second place, the reaction between the solution and the egg does not come about as directly as in my case. The accompanying table gives the data obtained with an emulsion of brain lecithin.

We may conclude, then, that the precipitation of lecithin by divalent kations is a physical phenomenon probably of an electrical nature, because:—

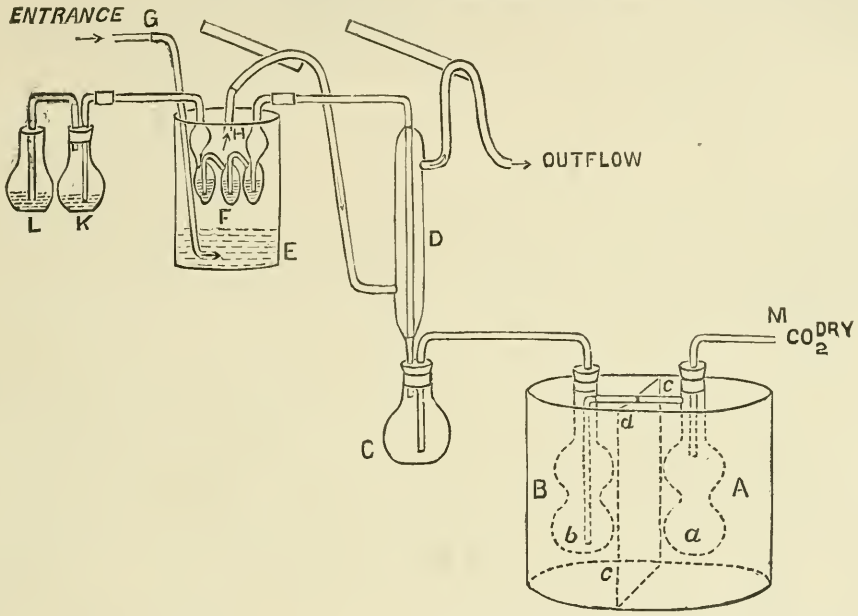
1. Non-electrolytes do not prevent the precipitation (I., VIII., IX.).

2. The trivalent kation Fe‴ is much more efficient in preventing the precipitation than a monovalent one like Na (II., VII.).

3. The precipitate is formed independent of the concentration of the lecithin, and can be re-dissolved by the addition of water.

The application of these observations to Loeb's results must be postponed until other lecithans have been more carefully studied.

					After three hours.
I.	5 c.c. *m*/200 emul. + 5 c.c. water	+	5 c.c. *m*/10 $Ca(NO_3)_2$..	Immediate ppt.	Ppt. settled.
II.	,, ,, ,, 5 *m* NaCl	+	5 c.c. *m*/10 $Ca(NO_3)_2$..	No ppt.	No ppt.
III.	,, ,, ,, *m*/10 NaCl	+	1·5 c.c. *m*/10 $Ca(NO_3)_2$..	No ppt.	No ppt.
IV.	,, ,, ,, *m*/10 NaCl	+	5 c.c. *m*/10 $Ca(NO_3)_2$..	Immediate ppt.	Ppt. settled.
V.	,, ,, ,, *m*/10 NaCl	+	3·5 c.c. *m*/10 $Sr(NO_3)_2$ ..	No ppt.	No ppt.
VI.	,, ,, ,, 2½ *m* KCl	+	5 c.c. *m*/10 $Ca(NO_3)_2$..	No ppt.	No ppt.
VII.	,, ,, ,, *m*/10 $FeCl_3$	+	5 c.c. *m*/10 $Ca(NO_3)_2$..	No ppt.	No ppt.
VIII.	,, ,, ,, urea conc. sol.	+	5 c.c. *m*/10 $Ca(NO_3)_2$..	Ppt. formed slowly.	Ppt. settled.
IX.	,, ,, ,, glucose conc. sol.	+	5 c.c. *m*/10 $Ca(NO_3)_2$..	Ppt. formed slowly.	Ppt. settled.



Chemical Properties.

The chemical properties of the lecithans depend on two groups in the molecule:—First, the fatty acids, and, second, the complex of which the nitrogen is a part. The phosphoric acid, although the nucleus and very important in the building up of the molecule, does not seem to enter into any reaction, except on the complete destruction of the lecithan; as Halliburton ("The Chemical Side of Nervous Activity," 1901, p. 87) has found the phosphorus to decrease in degenerating nerves only after the eighth day.

Each lecithan contains, according to Thudichum, two fatty acids in the molecule:—One—either palmitic, stearic, or margaric—does not impart any particular property to the compound; the other—oleic in the case of lecithin, kephalinic in the case of kephalin—gives to the molecule its distinctive character. This distinctive group is always unsaturated, will therefore add iodine, and bring about the reduction of osmic acid. Upon this group, then, depends the use of osmic acid as a stain for nervous tissues in histological technique. The value of osmic acid as a general test for fats depends on the fact that all fats in the body contain some oleates. Pure stearates and palmitates will not give the test. The darkening of the lecithans on exposure to the air is also dependent on this group. In the case of kephalin, the change on exposure to the air takes place so rapidly as to suggest an autoxidisable substance capable of activating oxygen. The guiacblue reaction, however, gives a negative result; and Thudichum (*op. cit.*, p. 128) has shown that kephalin exposed to an atmosphere of oxygen in a eudiometer will not decrease the volume of the gas. The change is probably due to an internal re-arrangement in the molecule, and takes place within the molecule of the fatty acid itself; as Thudichum (*Ibid.*, p. 149) obtained from kephalin an acid by saponification (kephalinic acid) which exhibited the same changes as the mother-substance.

Less apparent, but nevertheless important, are the changes which the molecules of the lecithans undergo in the complex which contains the nitrogen. Thus Halliburton (*op. cit.*, p. 50) has found the cholin to increase in the cerebro-spinal fluid as the result of general paralysis. For the quantitative investigation of the cholin or neurin, the methyl groups attached to the nitrogen seem especially useful, as Herzig and Meyer (*Monatshefte für Chem.*, vol. xv., p. 613) have devised a method by which such groups can be accurately determined. The description of the method is not easily accessible. I will therefore repeat it here, with such modifications as have been found useful, before going on to describe the results obtained with lecithans from various sources.

Herzig and Meyer's Determination of Methyl attached to Nitrogen.

The apparatus consists of a double glass bulb, 4 c.m. wide at the largest diameter and 2½ c.m. at the narrowest diameter, and 12 c.m. high. The bulb *a* is connected to *b* by a glass tube which runs to the bottom of *b*. The double bulbs are placed in an iron sand-bath with double bottom and a partition, *c d*, so that *a* can be heated in sand, while *b* remains comparatively cool. C is a flask for catching the distillation products from the bulbs, and D is a condenser kept at a temperature of from 40° to 50° C. E is a beaker into which the water enters at G, is heated to a temperature of from 40° to 50° C. by a Bunsen burner, and is drawn off by means of a syphon at H, to enter the condenser D and keep it at the proper temperature. By regulating the flow of the water and the height of the flame, the temperature of the water can easily be kept within the required limits. F are Geissler bulbs for absorbing everything but the methyl iodide, which is

absorbed in K and L. The analysis is carried on as follows:—0·2 g. of the substance to be analysed is placed in *a* with 2 g. of dry ammonium iodide and enough hydriodic acid (sp. gr. 1·6) to half fill the lower bulb. In *b* is placed 1 g. of ammonium iodide. The part A of the sand-bath is filled with sand, and a thermometer reading to 365° C. placed in the sand. A stream of dry CO_2 is allowed to enter at M, and when all the air is displaced, a triple burner is lighted under the sand-bath. In the meanwhile the water must be started and kept running through the condenser D at a temperature of from 40° to 50° C. As the temperature of 200° C. is reached in the sand-bath, methyl iodide begins to split off, and is carried over by the CO_2, mixed with hydriodic acid and iodine. Most of the iodine and hydriodic acid is condensed at D and collected in C. Some passes over and is absorbed in F, which contains the following solution:—

Sodium carbonate	1 part
Potassium arsenite	1 part
Water..	10 parts

The methyl iodide passes on and is collected in K, which contains 2 g. of silver nitrate dissolved in 5 c.c. water and 45 c.c. absolute alcohol. The methyl iodide dissolves in the alcohol, and is decomposed by the silver nitrate with the formation of silver iodide. After some time the temperature in the sand-bath gradually rises to 240° C., and after a little while longer methyl iodide ceases to come over, as can be seen by the liquid in K becoming perfectly clear. L, which also contains silver nitrate, is used merely as a guard. The solution can be removed at this point, and the silver iodide collected corresponds to all the kephalin and one methyl group of the lecithin. Fresh silver nitrate is placed in K, another burner placed under the sand-bath, and the temperature raised to 300° C. The remaining two methyl groups of lecithin come over, while kephalin gives off no more, or only a trace of methyl iodide. The second part of the sand-bath, B, is now filled with sand and heated to 300° to decompose anything which may have escaped previous heating. The two alcoholic solutions containing the silver iodide are diluted with much water and warmed for several hours on a steam-bath to remove alcohol. Strong nitric acid is then added, and the silver iodide filtered into a Gooch crucible and weighed. In case we are not dealing with a mixture of lecithans, all the silver iodide can be weighed in one portion.

(To be continued).

Reaction between Nitric and Hydriodic Acids.—Adolf Eckstadt.—The examination of the reaction which takes place between nitric and hydriodic acids offers numerous difficulties. The rapidity of the reaction is actually increased by the presence of germs, and towards the end of the reaction by the precipitation of colloidal iodine. It is further augmented by the oxidation of the products of the reduction of the nitric acid by the atmospheric oxygen. The author has examined the action of both nitrous and nitric acids on hydriodic acid. In the absence of air the former may be formulated as follows:—$(H_2)' + 1' + (NO_2)' = H_2O + I + NO$ or $N(OH)_3 + HI = NO + 2H_2O + I$. The second is represented by the equation $(NO_3)' + 2H' + 2I' = (NO_2)' + H_2O + 2I$ or $N(OH)_5 + 2HI = N(OH)_3 + 2H_2O + I_2$. The presence of ferrous ions certainly causes an acceleration of the reaction. This result may be interpreted by the help of the hypothesis of a ferro-hydriodic acid, an hypothesis analogous to that which serves to explain the reaction between permanganate and hydrochloric acid. The absence of all catalytic acceleration in the presence of the other metallic salts may be compared with the neutralising action of the manganese salts on the permanganate + HCl reaction. The salts on which the experiments have been carried out are the nitrates of the following metals:—K′, NH_4′, Be″, Ba″, Mg″, Zn″, Cd″, Ni″, Co″, Mn″, Fe″, Te_4O_7″, VO_2‴, Al‴, Cr‴, Fe‴, Th‴′ —*Zeit. Anorg. Ch.*, vol. xxix., p. 51.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, March 5th, 1903.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

(Concluded from p. 141).

39. "*The Rate of Decomposition of Diazo-compounds.* Part III. *The Temperature Coefficient.*" By J. C. CAIN and F. NICOLL.

The authors have determined the temperature coefficients by the use of Arrhenius's formula,—

$$C_{t_1} = C_{t_0} e^{A(T_1 - T_0) : T_1 T_0},$$

the values of C being calculated from the formula—

$$\frac{1}{t} \log \frac{A}{A - x} = C,$$

as indicated in their earlier communications (*Trans.*, 1902, lxxxi., 1412; 1903, lxxxiii., 206).

The values of A for diazobenzene-*p*-sulphonic acid and the chlorides of diazobenzene, diazo-*o*-toluene, diazo-*m*-toluene, diazo-*p*-toluene, and diazo-*m*-nitrobenzene do not vary much from each other, and agree with those found by Euler (*Annalen*, 1902, cccxxv., 301) for diazobenzene chloride (11905) and diazo-*p*-bromobenzene chloride (13634). By the use of the temperature coefficients thus obtained, the value of C at other temperatures has been calculated in several cases, and shown to be in agreement with the numbers found by other observers.

40. "*An Analysis of the Natural Gas at Heathfield, Sussex.*" By H. B. DIXON and W. A. BONE.

When the possibility of the industrial application of the Heathfield natural gas was brought before the Royal Commission on Coal Supplies, one of the authors (H. B. D., a member of the Commission) was asked to visit Heathfield and examine the nature of the gas on behalf of the Commission. Accordingly, several samples of gas were collected and sealed up in glass tubes on October 10th, 1902, and brought to Owens College for analysis.

According to Mr. Richard Pearson, Managing Director of the "Natural Gas Company," the gas was first discovered in 1836 in a well which was being sunk at Hawkhurst in West Sussex. In the Sub-Wealden boring (1873—1875), the gas was met with at Netherfield on the South Eastern Railway. Gas was first encountered at Heathfield in 1895 in sinking a well for water in the hotel yard, about 50 yards from the station. In 1896, the same firm of well sinkers met the gas at a depth of 300 feet in a shaft sunk for water at the station; no water was found, but the gas continued to escape, and was then used for lighting the station.

At the date of the above visit, six wells were either sunk or in course of being sunk, and gas had been encountered in all of them after the bores had penetrated through the 300 or 400 feet of surface bed of sandstone and marl which forms, according to Mr. Pearson, the impervious lid to the natural holder of gas.

The gas was issuing from the bore holes at a pressure of between 140 and 200 lbs. per square inch, and was being used to drive gas-engines and to light (with incandescent mantles) the station and a number of houses in the village. When lighted at an inch pipe at the mouth of a bore-hole, the gas burnt with a large flame giving a fairly good light, the flame being more luminous than that of fire-damp from coal mines. In an argand burner, the gas burnt with a moderately luminous flame, but gave little light in an ordinary bats-wing, so that it was difficult to understand how the gas could contain 5½ per cent of ethylene, as was stated, unless, indeed, the free oxygen, also said to be present, was sufficient to destroy its lighting power. The analyses, however, showed that neither ethylene nor free oxygen was present in the gas collected. To avoid the

possible loss of free oxygen by partial combustion in the tube while the drawn-out ends were being sealed, a sample was collected by closing the ends of the tube with paraffined indiarubber; it gave the same result.

The gas was transferred by means of a Töpler pump from the collecting vessels into small tubes standing over mercury. The analyses were made over mercury in a modified McLeod apparatus, all the reagents being freshly prepared.

A. *Preliminary examination for carbon dioxide, oxygen, unsaturated hydrocarbons, and carbon monoxide.*

1. The absence of carbon dioxide and oxygen was proved by exposing the gas successively to the action of (*a*) strong potassium hydroxide solution and (*b*) strongly alkaline pyrogallol solution. In neither case was there any appreciable absorption.

2. The absence of unsaturated hydrocarbons was shown in two separate experiments in which samples of gas were successively treated with (*a*) fuming sulphuric acid and (*b*) strong potassium hydroxide solution. No change in volume occurred in either experiment.

3. The gas always showed an appreciable contraction (as nearly as possible 1 per cent) when successively treated with ammoniacal cuprous chloride and dilute sulphuric acid. No precipitate of cuprous acetylide was formed. Since the foregoing experiments exclude the possibility of this contraction being due to oxygen or unsaturated hydrocarbons, it can only be attributed to the presence of carbon monoxide.

B. *Explosion analyses for saturated hydrocarbons, with, possibly, hydrogen, after removal of carbon monoxide.*

After removing the carbon monoxide from a considerable volume of the gas (by means of ammoniacal cuprous chloride and dilute sulphuric acid), the contraction, C, obtained on exploding measured volumes of the residual gas with a large excess of oxygen and air, was determined, and also the absorption, A, when the products of explosion were subsequently treated with strong potassium hydroxide solution. The following results were obtained:—

	1.	2.	3.
Volume of gas taken (corr.) .	48·25	55·70	58·75
Volume of oxygen and air added	457·45	468·30	465·45
C	94·35	109·10	115·20
A	48·25	55·90	58 80
C/A	1·956	1·952	1·959

C. *Proof that the gas does not contain free hydrogen.*

Before the foregoing results could be interpreted, it was necessary to ascertain whether the gas contained free hydrogen. This was done by exposing some of the gas, after removing carbon monoxide, to the action of "oxidised" palladium sponge at 100° for twenty minutes in an apparatus similar to that described by Bone and Jerdan (*Trans.*, 1901, lxxix., 1044), and afterwards redetermining the ratio C/A, when the residual saturated hydrocarbons were exploded with excess of oxygen and air. The results obtained were as follows:—

	4.	5.
Volume of gas taken (corr.)	62·3	55·3
Oxygen and air added..	472·5	493·0
C	121·8	108·2
A	62·2	55·4
C/A..	1·958	1·953

A comparison of these numbers with those given above shows clearly that the gas contains an appreciable quantity of free hydrogen. The five explosion analyses indicated, however, the presence, besides methane, of a small proportion of some higher saturated hydrocarbon, which is probably ethane. Assuming this to be the case, the percentage composition of the gas, after removing carbon monoxide, calculated from the five analyses, is as follows:—

	1.	2.	3.	4.	5.	Mean.
Methane	94·10	93·88	94·40	94·30	93·90	94·10
Ethane .	2·95	3·23	2·77	2·76	3·13	2·97
Nitrogen (by difference)	..	..	..	..	..	2·93
						100·00

The original gas, therefore, had the following composition:—

Carbon monoxide	1·00
Methane	93·16
Ethane	2·94
Nitrogen, or other inert gas (by difference)..	2·90
	100·00

41. "*Chemical Composition of Cooked Vegetable Foods.*" By Miss K. I. Williams.

The following constituents:—Water; total nitrogen (by Kjeldahl's method, modified to include the nitrogen of nitrates); ash; sulphur; phosphorus; cellulose (by Schulze's potassium chlorate method); woody fibre (by digestion with dilute sulphuric acid); carbohydrates convertible into dextrose; fat; and waste—were estimated in a series of vegetable foods including broccoli, Brussels sprouts, dried peas, oatmeal (coarse Scotch), and macaroni. These determinations being carried out on both the raw and the cooked materials.

42. "*The Density of Nitric Oxide.*" Preliminary Notice. By R. W. Gray.

It seemed doubtful whether nitric oxide had been obtained in a state of sufficient purity to admit of the accurate determination of its density and other physical constants. The value obtained by Leduc (*Comptes Rendus*, 1893, cxvi., 322) for the density does not agree absolutely with the value found by Victor Meyer and Daccomo (*Annalen*, 1887, ccxl., 326), while Olszewski's results (*Comptes Rendus*, 1885, c., 940) for the vapour pressures of the liquefied gas certainly suggest the possibility of impurity in the sample he used.

Nitric oxide, when prepared by many of the usual methods, contains small quantities of nitrous oxide and nitrogen. The higher oxides of nitrogen which are generated at the same time are apparently completely absorbed when passing through tubes containing potassium hydroxide in solution and in the solid form, and the gas then liquefies to a blue liquid which does not change in tint after repeated fractionation. The nitrogen present cannot be entirely removed by solidifying the nitric oxide by means of liquid air and pumping off the uncondensed gas; a small quantity remains behind in the solid nitric oxide, and can only be removed by liquefying and allowing a large portion of the liquid to boil away.

Owing to the ease with which liquid nitric oxide becomes superheated, it was found impossible to separate by fractionation the nitrous oxide present unless the upper part of the bulb containing the liquefied gas was kept below the melting temperature of solid nitrous oxide. When this was done, the densities of different fractions of the gas were found to agree.

The mean value for the weight of 1 litre of nitric oxide, prepared in two different ways, is 1·3402 grms. at 0° and 760 m.m. pressure (lat. Paris).

Until confirmed by further experiments, this value is not considered as final, but it is interesting to note that, assuming the truth of Avogadro's law for oxygen and nitric oxide under standard conditions of temperature and pressure, the ratio of the atomic weights so deduced for oxygen and nitrogen is 16 : 14·001.

The work is being continued with the object of making further experiments on the density of this gas and of determining its compressibility and other physical constants.

43. "*Hydrolysis of Urea Hydrochloride.*" By J. Walker and J. K. Wood.

A comparison method was described which permits the hydrolysis of a salt such as urea hydrochloride to be determined by the catalysis of cane sugar or methyl acetate with an error not exceeding 1 per cent; the results obtained with these two compounds being identical.

Within the limits 25—40°, temperature has practically no influence on the hydrolysis of urea hydrochloride.

The influence of dilution on the degree of hydrolysis x is expressed by the relation $\frac{x^2}{(1-x)v} = \text{constant}$.

The addition of sodium chloride very slightly diminishes the value of x.

The dissociation constant of urea, calculated from the hydrolytic experiments, is $1{\cdot}5 \times 10^{-14}$ at 25°.

44. "*The Affinities of some Feebly Basic Substances.*" By J. K. Wood.

By means of the methyl acetate method, together with some solubility experiments, the author has obtained the following results at 40·2°:—

Base.	Percentage hydrolysis of hydrochloride in decinormal solution.	Dissociation constant.
Creatinine	8·96	$3{\cdot}57 \times 10^{-11}$
Acetoguanamine	9·8	2·96 ,,
Semicarbazide	10·4	2·61 ,,
Glycocyamine	11·0	2·32 ,,
Creatine	12·3	1·81 ,,
Guanine	17·9	0·81 ,,
Acetonesemicarbazone	26·9	0·32 ,,
Acetoxime	34·3	0·175 ,,
Aminocaffeine	55·0	0·047 ,,
Theobromine	73·0	0·016 ,,
Dimethylpyrone	85·0	0·0065 ,,
Xanthine	88·5	0·0046 ,,
Acetanilide	88·9	0·0044 ,,
Caffeine	89·7	0·0040 ,,
Urea	90·4	0·0037 ,,
Acetamide	91·3	0·0033 ,,
Nitroguanidine	94·0	0·0021 ,,
Propionitrile	97	—
Cyneol	98	—
Biuret	>99	—
Benzamide	>99	—

PHYSICAL SOCIETY.

Ordinary Meeting, March 13th, 1903.

Dr. R. T. Glazebrook, F.R.S., President, in the Chair.

A paper by Dr. Farr, "*On the Interpretation of Milne Seismograms*," was read by Dr. Chree.

Professor Milne and Dr. Omiri have come to the conclusion that the tilts represented by the maximum displacement of the boom of a horizontal pendulum seismograph are too large to be admissible as true tilts. The author has investigated the motion of the boom analytically, and his results show:—(1) That the boom does not vibrate with its own natural period, but takes the frequency of the disturbing force; (2) that the friction should be small compared with the difference of the squares of the frequencies; and (3) that the phenomenon of beats may occur between the forced vibration and the free period of the boom. The maximum amplitude of swing of the boom gives no information whatever of the amplitude of the disturbing cause without also a knowledge of the periods of the forced and free vibrations. The author shows how to determine the amplitude of the wave by observations on these quantities. The author has verified the results of his analysis by experiments with artificial waves of known periods produced by an apparatus described in the paper. In conclusion, it appears (1) that strict attention should be paid to accurately recording the period of free vibration of the boom; (2) that the tape should be driven at such a speed as to enable the period of forced vibration to be determined; (3) that the effect of friction should be recorded.

The Chairman said the paper brought out clearly the possibility of interference between the periods of the boom and the earthquake tremors.

Prof. Perry said that, if possible, the period of the pendulum should be very different to that of the wave. The period might be made very great or excessively small, but there would probably be difficulties in either case.

Prof. Everett said it was obvious that the records could not easily be interpreted unless there was a great difference between the periods. He suggested the use of two booms having different periods.

Dr. Watson pointed out that the boom would respond equally well to any period if it was heavily damped. Fluid damping was unsatisfactory because of convection currents, and he suggested that the plate at the end of the boom should be made of copper and allowed to move between the poles of a strong horseshoe magnet.

Dr. Chree said that if the period of the boom was increased beyond eighteen seconds, the apparatus became too sensitive, and was unstable.

"*A Potentiometer for Thermocouple Measurements*" was exhibited and described by Dr. Lehfeldt.

To make a satisfactory potentiometer for thermoelectric work, it is essential that it shall not introduce a high resistance in the circuit of the couple and galvanometer. Most of the potentiometers on the market, though good enough for comparing voltaic cells, fail in this respect. Dr. Lehfeldt has therefore designed an instrument specially suited for thermocouple work. From the positive terminal of an accumulator a current flows to a switch, by means of which it can be sent through 100, 1000, or 10,000 ohms in order to get three grades of sensitiveness; it then passes through 20 coils of 0·1 ohm each, a slide-wire of a little more than 0·1 ohm, and through an adjustable resistance back to the accumulator. The fixed resistance of 100, 1000, or 10,000 ohms is shunted by a cadmium cell and a galvanometer, and the adjustable resistance varied until balance is obtained. The thermocouple and the galvanometer are then put across any number of the tenth-ohm coils, and any fraction of the slide-wire. Great care has been taken to avoid accidental thermo E.M.F.'s, which are the chief trouble in using thermocouples. The only metals used in the measuring-circuit are copper and manganin. The position of the sliding-contact upon the bridge-wire can be read by means of a vernier to $\frac{1}{10}$ m.m. corresponding to $\frac{1}{2000}$ of the unit employed, which may be 1000, 100, or 10 microvolts according to the fixed resistance used. The paper concludes with a description of the calibration of the various parts of the instrument and of the precautions to be taken when using it.

Dr. J. A. Harker exhibited and described "*A Direct-reading Potentiometer for Thermoelectric Work.*"

The instrument represents a form which has been designed and made in the National Physical Laboratory. Dr. Harker has experienced similar difficulties to Dr. Lehfeldt, and the instrument which he has designed is similar in many respects to the one described in the previous paper. The main current from an accumulator flows through a series of resistances, any one of which can be short-circuited at will, and then through the balancing-coils. By means of the adjustable resistance the standard cell employed can easily be made to cut off from the main circuit a resistance numerically equal to 100 times its E.M.F., and therefore 1 ohm on the potentiometer-circuit is equal to $\frac{1}{100}$ volt, always. The balancing-coils consist of 20 coils of 0·1 ohm each in series with 11 coils of 0·01 ohm each. Any two of these latter coils can be put in parallel with a slide-wire of 0·02 ohm resistance. The slide-wire is provided with a scale of 200 divisions, and as the fall along the wire is 100 microvolts, 0·1 microvolt can

easily be estimated. The slide-wire acts as a vernier to the small coils. Copper and manganin are the only metals used, and the connections are made by means of mercury cups.

Mr. W. A. PRICE said there was a great similarity between all forms of potentiometers. Electrically they were the same, but they differed mechanically. He referred to the large number of coils requiring calibration in the instruments exhibited. In working with sliding-contacts in a dusty workshop, it is an advantage to immerse the bridge in paraffin oil. The contacts are then always good, instead of uncertain and intermittent. He had also found that if two silver surface plates were screwed together, the contact-resistance was less when they were immersed in paraffin than when they were in air.

Mr. WHIPPLE said he had also found that contact-resistances in oil were less than in air, The oil acts as a lubricator, keeps the temperature constant, and the wires wear less.

Dr. WATSON said the effect of the oil seemed to depend upon the shape of the surfaces in contact, or it ought to be an advantage to grease the plugs of resistance-boxes. After what Mr. Price had said with regard to the contact-resistance of two pieces of silver, it would be interesting to work with a resistance-box in which the plugs were immersed in paraffin oil.

Prof. EVERETT expressed his interest in the fact that an insulating material, such as paraffin, should decrease the contact-resistance between two metals. He suggested that the paraffin drives off the film of air from the metals.

Dr. HARKER asked Dr. Lehfeldt if he had worked with all three sensitivities, and pointed out that the middle one was the same as that adopted in his own instrument.

Dr. LEHFELDT said that for small voltages he used the highest sensitivity. Inequalities in the slide-wire amounted to about $\frac{1}{10}$ m.m. of wire. The open scale in Dr. Harker's instrument was convenient in place of a vernier.

A paper on "*The Measurement of Small Resistances*" was read by Mr. A. CAMPBELL.

The object of this paper is to give a brief account of a number of measurements of a set of low resistance standards belonging to the National Physical Laboratory. The tests were made partly with a view to comparing various methods of measurement. The resistances were of manganin, and their nominal values were approximately 0·1, 0·01, 0·001 international ohms. The following methods were employed :—(1) Shunt potentiometer; (2) Kelvin bridge; (3) two-step bridge; (4) differential galvanometer; (5) Matthiessen's and Hockin's method. The last method was found to be much less accurate than the other four. The results obtained from the other methods are tabulated in the paper, and show very satisfactory agreement.

Dr. R. A. LEHFELDT read a paper on "*A Resistance Comparator.*"

Objecting to sliding-contacts on account of the thermo-electric effects they tend to introduce, and irregularities slide-wires show when a good deal used, the author has substituted for the slide-wire two coils of 99 ohms each connected by 20 coils of 0·1 ohm each. The latter are arranged circularly, so that a switch connected to the galvanometer may be set on any one of the intervening studs. The galvanometer deflections are taken for the two positions nearest balance and interpolation to $\frac{1}{100}$ calculated. In this way an accuracy of one part in 100,000 is attainable. The author thinks there is a gain of accuracy as well as of convenience in using the interpolation method.

The Thio-acids, RCOSH.—V. Auger and M. Billy.—The authors use Kekulé's method for obtaining the salts of the thio-acids by saponification of NaHS, and they find that the ether salts contain an alcohol group always giving mercaptans.—*Comptes Rendus*, cxxxvi., No. 9.

NOTICES OF BOOKS.

The Physical Papers of Henry Augustus Rowland, Ph.D., LL.D., Professor of Physics and Director of the Physical Laboratory in the Johns Hopkins University, 1876-1901. Collected for Publication by a Committee of the Faculty of the University. Baltimore: The Johns Hopkins Press. 1902. Pp. 704.

IN deciding on the scope of this volume, which has been compiled as a Memorial to the late Professor Rowland, the Committee appointed to arrange the matter decided to include only the distinctly Physical papers.

Professor Rowland's first published paper was a letter to *The Scientific American* in 1865, when he was only sixteen years of age. He himself declared that he did not expect it to be published, having written it for a joke. The subject chosen was "The Vortex Problem." His first paper of importance was "On Magnetic Permeability, and the Maximum of Magnetism of Iron, Steel, and Nickel," published in the *Philosophical Magazine* in the year 1873. The value of this paper was at once recognised by European physicists, and Rowland at once took high rank as an investigator, in Europe at any rate.

Important papers on electrical and magnetic subjects followed rapidly, and these included many of practical value besides those of purely theoretical interest.

But electricity was not the only subject touched by this gifted investigator; his papers on heat and light are well known, and those connected with the practical manufacture of gratings for optical purposes are of world-wide renown. The great fault in gratings, up to the time when Rowland took the matter up, was want of uniformity in spacing. He saw, as others had seen before him, that the dominating element of a ruling-machine was the screw by means of which the cutting tool or plate was moved along. The ruled plate would repeat all the irregularities of the screw, and the problem was to make a screw which would be practically free from periodic and other errors. He was not long in devising a method, that of grinding, which astonished everybody by its simplicity and almost absolute perfection of its results; indeed, the very first screw made by this process still ranks as the most perfect in the world.

As a chemist, Professor Rowland carried on investigations for several years on the so-called "rare earths," such as yttrium, erbium, cerium, &c., and devised several methods for their separation; the paper in which he published these results was printed in the *Johns Hopkins University Circulars*, 1894, No. 112, p. 73.

Towards the end of this volume there are given six Addresses read before different societies between 1883 and 1900; and the last paper of all is an illustrated description of the dividing engines designed by Professor Rowland.

There are altogether seventy papers and addresses included in this volume, and they form a lasting memorial of the untiring energy and genius of their writer. The book is well printed in large type, well bound, and as a frontispiece contains an excellent portrait of the originator of all it holds.

Principles of Inorganic Chemistry. By HARRY C. JONES. Associate Professor of Physical Chemistry in the Johns Hopkins University. New York: The Macmillan Company. London; Macmillan and Co., Ltd. 1903. Pp. 521.

DURING recent years the theory of inorganic chemistry has undergone modifications; it is becoming more mathematical, and several new generalisations have been added to those already known. The more important of these generalisations are:—The theory of electrolytic dissociation, the law of mass action, the phase rule, and Faraday's law as the basis of chemical valence. The

importance of ions in chemical reactions has become more widely recognised, and this, says the author, necessitates a fundamental change in our conceptions of chemical phenomena. The application of Faraday's law as the basis of chemical valence is not new, but the importance of the application has only recently become apparent. The importance of ions, which are charged atoms or groups of atoms, and the study of electro-chemical phenomena in general, have made prominent the fact that the law of Faraday is a fundamental law of chemistry as well as of physical chemistry.

It must not be supposed, however, that the author abandons the older ideas; on the contrary, his aim is to add to the older generalisations those recently discovered, and to combine them into a harmonious whole.

The book, which is a large one, is divided into forty-one chapters, the greater number of which are devoted to the study of individual elements, or groups of closely allied elements, and their compounds; the first two chapters being devoted to the relations between chemistry and physics, the number of chemical elements, and generalisations, such as the law of mass, the laws of constant and multiple proportion, the correlation and conservation of energy, &c.

Chapter VIII. is an important one, on osmotic pressure and the theory of electrolytic dissociation. It is only in the past two or three years that the subject of osmotic pressure has come into prominence, although its existence has been long recognised; but in the hands of certain workers, such as van't Hoff, it has thrown a good deal of light on chemical phenomena in general. Van't Hoff has been followed up by Arrhenius, and he has satisfactorily solved the problem of the large number of exceptions to the generalisations reached by van't Hoff connecting gas-pressure and osmotic pressure. The new feature introduced by Arrhenius was to point out a method for determining just what per cent of the molecules is broken down into ions, and he thus converts a purely qualitative suggestion into a quantitative theory, which could be tested experimentally.

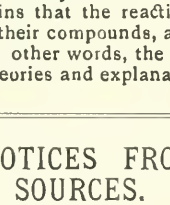
This theory is the governing idea of the rest of the book, and though some may hesitate before accepting it, the broad fact remains that the reactions and properties of the elements and their compounds, as herein described, remain as before; in other words, the chemistry remains the same, but the theories and explanations are amplified.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 9, March 2, 1903.

Preparation and Properties of the two Tetra-alcoyldiamidodiphenylanthrones.—A. Haller and A. Guyot.—Under the name of diphenylanthrone the authors described some time ago a compound, $C_{26}H_{18}O$, obtained by condensation of di-symmetric phthalyl tetrachloride with benzine in presence of aluminium chloride. This compound has since been prepared by several methods, and is found to have the formula—



Amongst its derivatives are the dialcoylamidodiphenylanthrones, which the author now investigates.

Heat of Combustion of Phosphorus. Phosphoric Anhydrides.—H. Giran.—The author measures the heat of combustion of white phosphorus in Mahler's calorimeter in presence of oxygen under a pressure of 15 or 20 atmospheres, and +369 4 cals. is the number obtained. He also measures the heat of solution of the anhydride obtained in the same experiments, +34·37 cals. On the other hand, when the three varieties of phosphoric anhydride are dissolved in water the numbers obtained are—

P_2O_5 cryst. + aq = P_2O_5 diss. +40·79 cals.
P_2O_5 amorph. + aq = P_2O_5 ,, +33·81 ,,
P_2O_5 vitreous + aq = P_2O_5 ,, +29·09 ,,

From this it can be shown that white phosphorus burnt under the above conditions gives the amorphous variety of oxide. Finally, the author obtains a means of calculating the quantity of heat evolved during the reciprocal transformations from one variety into another.

New Acetylenic Acids.—Ch. Moureu and R. Delange.—Up to the present, only a small number of the acetylenic acids, $R-C\equiv C-CO_2H$ have been prepared, and their chemical history is very incomplete, owing no doubt to the difficulty of their preparation. In order to investigate the properties of this series of acids, the author prepares a number of them, including many new ones, by the following method:—Carbonic anhydride is fixed on to the sodium derivative of the acetylenic hydrocarbon, $R-C\equiv CNa$. In this manner ethers of the acids can be obtained by treating the same sodium derivatives with chlorocarbonic ethers. The following is a list of acids prepared:—

Propylpropiolic acid, $CH_3-CH_2-CH_2-C\equiv C-CO_2H$.
Isopropylpropiolic acid, $(CH_3)_2CH-C\equiv C-CO_2H$.
Butylpropiolic acid,—
$CH_3-CH_2-CH_2-CH_2-C\equiv C-CO_2H$.
Trimethyltetrolic acid, $(CH_3)_3C-C\equiv C-CO_2H$.
Amylpropiolic acid, $CH_3-(CH_2)_4-C\equiv C-CO_2H$.
Isoamylpropiolic acid,—
$(CH_3)_2CH-CH_2-CH_2C\equiv C-CO_2H$.
Hexylpropiolic acid, $CH_3-(CH_2)_5-C\equiv C-CO_2H$.
Isohexylpropiolic,—
$(CH_3)_2CH-CH_2-CH_2-CH_2-C\equiv C-CO_2H$.
Heptylpropiolic, $CH_3-(CH_2)6-C\equiv C-CO_2H$.
Nonylpropiolic, $CH_3-(CH_3)8-C\equiv C-CO_2H$.

Paraethylbenzoic Aldehyde.—H. Fournier.—*p*-Ethylbenzoic aldehyde, $C_6H_4{<}^{C_2H_5\ (1)}_{CHO\ (4)}$, can be prepared by various methods. The author makes a careful preparation in order to fix the constitution of the acid. The substance is heated with concentrated sulphuric acid and precipitated by water. Paraethylbenzoic acid separates, fusing at 113°. After this, the acid fusible at 71° separates, which is paraethylbenzeneketocarbonic acid, $C_6H_4{<}^{C_2H_5}_{COCO_2H}$.

MISCELLANEOUS.

"The Machinery Users' Journal," Vol. I., No. 1.—We have received an advance copy of this new journal, which is just making its appearance. It appears to be of rather a political character, inasmuch as it proposes to keep a close watch upon proceedings in Parliament, and will advise its readers when it is necessary to bring pressure upon the Government, or to lay their views before Committees of either House. Proposals of the Government in respect of taxation, private bill legislation, attempts to still further regulate and control industry, will, in particular, be carefully examined. The journal will not concern itself with subjects which are already adequately dealt with in other periodicals or trade organs, but reviewing all the complex conditions which govern industry in a modern State, it will advise its readers, month by

month, what steps they should take to safeguard or advance their interests. Among the questions it is proposed to consider we may mention the pollution of rivers, rating of machinery, disposal of trade effluents, water supplies, municipal trading, labour organisations, &c., and the journal will seek rather to influence than to merely record events.

The Paper Trade Directory of Great Britain for 1903.—In this Directory will be found the addresses, not only of those who produce paper in the ordinary acceptance of the word, but also of those who manufacture paper-boards for various building purposes, both waterproof and fireproof; paper barrels, kegs and drums; asbestos paper and boards; imitation leather papers and boards; and, we are sorry to see, insoles and other articles for the boot and shoe trade. The book is published at the offices of *Paper Making*, and is compiled and edited by the editor of that journal.

The Roasting of Fluorised Blendes.—E. Prost and E. Lecoq.—On account of its attacking the crucibles, the fluorine contained in blende is very inconvenient in the manufacture of zinc. The roasting of the blende gets rid of a part of it, and it is important to find out under what conditions this loss is at its maximum. When we roast one of these minerals in a current of air, and collect the products of the roasting in water, we observe the production of gelatinous silica, indicating the presence of fluoride of silicon. From comparative assays made on different samples, more or less rich in silica or in fluorine, we see that up to a certain point the silica helps the removal of the fluorine. On the other hand, the heating of fluorine, mixed with oxide of lead, zinc, or iron, does not give rise to any evolution of fluorine. By calcining fluorised minerals in a current of steam we probably obtain the disengagement of a part of the fluorine in the form of hydrofluoric acid.—*Bull. Assoc. Belge Chim.*, vol. xv., No. 2, p. 99.

Action of Nitrate of Copper on Benzene.—N. Vassilief.—The author used very pure benzene free from thiophene and nitrate of copper, $Cu(NO_3)_2.3H_2O$. These two bodies react, one on the other, as soon as the temperature reaches 100°, but the reaction is very slow at first; it is much better to heat in sealed tubes at 170—190° for twelve or eighteen hours. The products of the reaction are numerous; the author has detected, up to the present, picric acid, benzoic acid, and an acid having the composition $C_nO_{2n}H_{2n-2}$; but there are still other compounds not yet examined. At the end of the operation we find in the tubes a lower oily layer, and above that an aqueous layer containing insoluble matters; these latter consist of a basic nitrate of copper, and a salt of copper with the acid $C_nH_{2n-2}O_{2n}$; these three salts are separated with nitric acid of 1·2 density, which dissolves the first and does not affect the second; the third one, placed in suspension in water, is decomposed by sulphuretted hydrogen, and the solution concentrated on the water-bath; at the ordinary temperature it deposits the crystallised acid. This body is very soluble in water, less so in alcohol, and very slightly in ether. In open tubes it does not melt with heat, but decomposes slowly; in sealed tubes it melts at 98–100°, but with partial decomposition, as a pressure is observed due to carbonic acid. The copper salt of this acid is a greenish powder; the silver salt, which curdles as soon as it is precipitated, changes into a yellowish white powder, and detonates when heated; they are both stable with mineral acids, especially hydrochloric and nitric. The acid, heated with hydrochloric acid and alcohol, gives oxalic ether. It is certainly not oxalic acid, for its salts differ from the oxalates, especially those of ammonia and phenylhydrazine; this latter is completely insoluble in water, and only slightly soluble in boiling alcohol; it melts at 175—176° with decomposition. Neither is the acid in question dioxymalonic acid or dioxysuccinic; in fact, it has not been identified with any known acid; the author is continuing its examination.—*Journ. Soc. Phys. Chim. R.*, vol xxxiv., p. 33.

MEETINGS FOR THE WEEK.

Tuesday, 31st.—Royal Institution, 5. "Great Problems in Astronomy," by Sir Robert Ball, F.R.S.

—— Society of Arts, 4.30. "British North Borneo," by Henry Walker, Commissioner of Lands, British North Borneo.

Wednesday, April 1st.—Society of Arts, 8. "Application of Polyphase Motors to the Electrical Driving of Workshops and Factories," by Alfred C. Eborall, M.I.E.E.

Thursday, 2nd.—Royal Institution, 5. "Society during the Commonwealth and Protectorate," by Charles Harding Firth, M.A.

—— Chemical, 8. "On the Absorption Spectra of Nitric Acid in various States of Concentration," by W. N. Hartley. "The Dioximes of Camphorquinone and other Derivatives of *iso*-Nitrosocamphor," by M. O. Forster. "Salts of a Mercaptoid Isomeric Form of Thioallophanic Acid, and a New Synthesis of Iminocarbaminethioalkyls," by A. E. Dixon. "Discoloured Rain," by E. G. Clayton. "Derivatives of *o*-Aminobenzophenone and *p*-Aminobenzophenone," by F. D. Chattaway.

Friday, 3rd.—Royal Institution, 9. "Drops and Surface Tension." by Lord Rayleigh, F.R.S., &c.

Saturday, 4th.—Royal Institution, 3. "Light—its Origin and Nature," by Lord Rayleigh, F.R.S., &c.

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THE CHEMICAL NEWS.

Vol. LXXXVII., No. 2262.

THE EMANATIONS OF RADIUM.*

By Sir WILLIAM CROOKES, F.R.S.

A solution of almost pure radium nitrate which had been used for spectrographic work, was evaporated to dryness in a dish, and the crystalline residue examined in a dark room. It was feebly luminous.

A screen of platinocyanide of barium brought near the residue glowed with a green light, the intensity varying with the distance separating them. The phosphorescence disappeared as soon as the screen was removed from the influence of the radium.

A screen of Sidot's hexagonal blende (zinc sulphide), said to be useful for detecting polonium radiations, was almost as luminous as the platinocyanide screen in presence of radium, but there was more residual phosphorescence, lasting from a few minutes to half an hour or more according to the strength and duration of the initial excitement.

The persistence of radio-activity on glass vessels which have contained radium is remarkable. Filters, beakers, and dishes used in the laboratory for operations with radium, after having been washed in the usual way, remain radio-active; a piece of blende screen held inside the beaker or other vessel immediately glowing with the presence of radium.

The blende screen is sensitive to mechanical shocks. A tap with the tip of a pen-knife will produce a sudden spark of light, and a scratch with the blade will show itself as an evanescent luminous line.

A diamond crystal brought near the radium nitrate glowed with a pale bluish-green light, as it would in a "Radiant Matter" tube under the influence of cathodic bombardment. On removing the diamond from the radium it ceased to glow, but, when laid on the sensitive screen, it produced phosphorescence beneath which lasted some minutes.

During these manipulations the diamond accidentally touched the radium nitrate in the dish, and thus a few imperceptible grains of the radium salt got on to the zinc sulphide screen. The surface was immediately dotted about with brilliant specks of green light, some being a millimetre or more across, although the inducing particles were too small to be detected on the white screen when examined by daylight.

In a dark room, under a microscope with a $\frac{2}{3}$-inch objective, each luminous spot is seen to have a dull centre surrounded by a luminous halo extending for some distance around. The dark centre itself appears to shoot out light at intervals in different directions. Outside the halo the dark surface of the screen scintillates with sparks of light. No two flashes succeed one another on the same spot, but are scattered over the surface, coming and going instantaneously, no movement of translation being seen.

The scintillations are somewhat better seen with a pocket lens magnifying about 20 diameters. They are less visible on the barium platinocyanide than on the zinc sulphide screen.

A powerful electro-magnet has no apparent effect on the scintillations, which appear quite unaffected when the current is made or broken, the screen being close to the poles, and arranged axially or equatorially.

A solid piece of radium nitrate is slowly brought near the screen. The general phosphorescence of the screen as visible to the naked eye varies according to the distance of the radium from it. On now examining the surface with the pocket lens, the radium being far off and the screen faintly luminous, the scintillating spots are sparsely scattered over the surface. On bringing the radium nearer the screen the scintillations become more numerous and brighter, until when close together the flashes follow each other so quickly that the surface looks like a turbulent luminous sea. When the scintillating points are few there is no residual phosphorescence to be seen, and the sparks succeeding each other appear like stars on a black sky. When, however, the bombardment exceeds a certain intensity, the residual phosphorescent glow spreads over the screen, without, however, interfering with the scintillations.

If the end of a platinum wire which has been dipped in a solution of radium nitrate and dried is brought near the screen, the scintillations become very numerous and energetic, and cease immediately the wire is removed. If, however, the end of the wire touches the screen, a luminous spot is produced which then becomes a centre of activity, and the screen remains alive with scintillations in the neighbourhood of the spot for many weeks afterwards.

"Polonium" basic nitrate produces a similar effect on the screen, but the scintillations are not so numerous.

Microscopic glass, very thin aluminium foil, and thin mica do not stop the general luminosity of the screen from the X-rays, but arrest the scintillations.

I could detect no variation in the scintillations when a rapid blast of air was blown between the screen and the radium salt.

A beam of X-rays from an active tube was passed through a hole in a lead plate on to a blende screen. A luminous spot was produced on the screen, but I could detect no scintillations, only a smooth, uniform phosphorescence. A piece of radium salt brought near gave the scintillations as usual, superposed on the fainter phosphorescence caused by the X-rays, and they were not interfered with in any degree by the presence of X rays falling on the same spot.

During these experiments the fingers soon become soiled with radium, and produce phosphorescence when brought near the screen. On turning the lens to the, apparently, uniformly lighted edge of the screen close to the finger, the scintillations are seen to be closer and more numerous; what to the naked eye appears like a uniform "milky way," under the lens is a multitude of stellar points, flashing over the whole surface. A clean finger does not show any effect, but a touch with a soiled finger is sufficient to confer on it the property. Washing the fingers stops their action.

It was of interest to see if rarefying the air would have any effect on the scintillations. A blende screen was fixed near a flat glass window in a vacuum tube, and a piece of radium salt was attached to an iron rocker, so that the movement of an outside magnet would either bring the radium opposite the screen or draw it away altogether. A microscope gave a good image of the surface of the screen, and in a dark room the scintillations were well seen. No particular difference was observed in a high vacuum—indeed, if anything, the sparks appeared a trifle brighter and sharper in air than *in vacuo*. A duplicate apparatus in air was put close to the one in the vacuum tube, so that the eye could pass rapidly from one to the other, and it was so adjusted that the scintillations were about equal, when each was in air. The vacuum apparatus was now exhausted to a very high point, and the appearance on each screen was noticed. Here, again, I thought the sparks in the vacuum were not quite so bright as in air, and on breaking the capillary tube of the pump and observing as the air entered, the same impression was left on my mind; but the differences, if any, are very minute, and are scarcely greater than might arise from errors of observation.

It is difficult to form an estimate of the number of flashes of light per second. But with the radium at about five centims. off the screen they are barely detectable,

* A Paper read before the Royal Society, March 19, 1903.

not being more than one or two per second. As the distance of the radium diminishes the flashes become more frequent, until at one or two centims. they are too numerous to count.

On bringing alternately a Sidot's blende screen and one of barium platinocyanide face downwards near a dish of "polonium" sub-nitrate, each became luminous, the blende screen being very little brighter of the two. On testing the two screens over a crucible containing dry radium nitrate, both glowed; in this case the blende screen being much the brighter. Examined with a lens, the light of the blende screen was seen to consist of a mass of scintillations, while that of the platinocyanide screen was a uniform glow, on which the scintillations were much less apparent.

The screens were now turned face upwards, so that emanations from the active bodies would have to pass through the thickness of card before reaching the sensitive surface. Placed over the "polonium" neither screen showed any light. Over the radium the platinocyanide screen showed a very luminous disc, corresponding with the opening of the crucible, but the blende disc remained quite dark.

It therefore appears that practically the whole of the luminosity on the blende screen, whether due to radium or "polonium," is occasioned by emanations which will not penetrate card. These are the emanations which cause the scintillations, and the reason why they are distinct on the blende and feeble on the platinocyanide screen, is that with the latter the sparks are seen on a luminous ground of general phosphorescence which renders the eye less able to see the scintillations.

Considering how coarse-grained the structure of matter must be to particles forming the emanations from radium, I cannot imagine that their relative penetrative powers depend on difference of size. I attribute the arrest of the scintillating particles to their electrical character, and to the ready way in which they are attracted by the coarser atoms or molecules of matter. I have shown that radium emanations cohere to almost everything with which they come into contact. Bismuth,* lead, platinum, thorium, uranium, elements of high atomic weight and density, possess this attraction in a high degree, and only lose the emanations very slowly, giving rise to what is known as "induced radio-activity." The emanations so absorbed from radium by bismuth, platinum, and probably other bodies, retain the property of producing scintillations on a blende screen, and are non-penetrating.

It seems probable that in these phenomena we are actually witnessing the bombardment of the screen by the electrons† hurled off by radium with a velocity of the order of that of light; each scintillation rendering visible the impact of an electron on the screen. Although, at present, I have not been able to form even a rough approximation to the number of electrons hitting the screen in a given time, it is evident that this is not of an order of magnitude inconceivably great. Each electron is rendered apparent only by the enormous extent of lateral disturbance produced by its impact on the sensitive surface, just as individual drops of rain falling on a still pool are not seen as such, but by reason of the splash they make on impact, and the ripples and waves they produce in ever-widening circles.

Announcement.—Mr. Bertram Blount announces that owing to the death of his late partner, Mr. W. Harry Stanger, the firm of Stanger and Blount is dissolved. The business of the late firm is being temporarily conducted at 2, Broadway, Westminster, but at an early date Mr. Blount will remove to other premises in Westminster.

* I have been quite unable to detect any lines but those of bismuth (and of known impurities) in the spectrum of the strongest and most active "polonium" salt I have been able to procure.

† Radiant matter, satellites, corpuscles, nuclei; whatever they are, they act like material masses.

THE MYSTERY OF RADIUM.

By Sir WILLIAM CROOKES, F.R.S.

The following letter appeared in *The Times* of March 26th:—

Sir,—In the presence of a mystery like that of Radium any reasonable attempt at explanation will be welcome, so I will ask your permission to revive a hypothesis I ventured to submit to the British Association in my Presidential Address in 1898. Speaking of the radio-active bodies then just discovered by M. and Mdme. Curie, I drew attention to the large amount of energy locked up in the molecular motions of quiescent air at ordinary pressure and temperature, which, according to some calculations by Dr. Johnstone Stoney, amounts to about 140,000 foot-pounds in each cubic yard of air; and I conjectured that radio-active bodies of high atomic weight might draw upon this store of energy in somewhat the same manner as Maxwell imagined when he invented his celebrated "Demons" to explain a similar problem. I said it was not difficult so to modify this hypothesis as to reduce it to the level of an inflexible law, and thus bring it within the ken of a philosopher in search of a new tool. I suggested that the atomic structure of radio-active bodies was such as to enable them to throw off the slow-moving molecules of the air with little exchange of energy, while the quick-moving missiles would be arrested, with their energy reduced and that of the target correspondingly increased. (A similar sifting of the swift-moving molecules is common enough, and is effected by liquids whenever they evaporate into free air). The energy thus gained by the radio-active body would raise its temperature, while the surrounding air would get cooler. I suggested that the energy thus gained by the radio-active body was employed partly in dissociating some of the gaseous molecules (or in inducing some other condition which would have the effect of rendering the neighbouring air a conductor of electricity) and partly in originating undulations through the ether, which, as they take their rise in phenomena so disconnected as the impacts of molecules, must furnish a large contingent of Stokesian pulses of short wave-length. The shortness in the case of these waves appears to approach, without attaining, the extreme shortness of ordinary Röntgen rays.

Although the fact of emission of heat by Radium is in itself sufficiently remarkable, this heat is probably only a small portion of the energy Radium is constantly sending into space. It is at the same time hurling off material particles which reveal their impact on a screen by luminous scintillations. Stop these by a glass or mica screen and torrents of Röntgen rays still pour out from a few milligrms. of Radium salt, in quantity to exhibit to a company all the phenomena of Röntgen rays, and with energy enough to produce a nasty blister on the flesh, if kept near it for an hour.

In conclusion, if it is not too much trespassing on your space, I should like to express the great admiration which I have, in common with all English men of science, at the brilliant discovery of Radium, and its unique properties—the crowning point of the long and painstaking series of researches on radio-active bodies undertaken by Professor Curie and his talented coadjutor, Mdme. Curie.

I remain, Sir, your obedient servant,

WILLIAM CROOKES.

Society of Arts.—The following are the arrangements for the Wednesday evening meetings of the Society of Arts after Easter:—April 22.—"Modern Bee Keeping," by Walter Francis Reid, F.C.S. April 29.—"Automatic Wagon Couplings," by T. A. Brockelbank. May 6.—"The Construction of Maps and Charts," by G. T. Morrison. May 13.—"Preservation of Big Game in Africa," by E. North Buxton. May 20.—"Fencing as an Art and an Historic Sport," by Egerton Castle, M.A.

HEAT EVOLVED BY RADIUM SALTS.

By P. CURIE and A. LABORDE.

WE have already proved that radium salts give out heat continuously. A thermo-electric couple, in which one junction is surrounded by radiferous barium chloride and the other by pure barium chloride, registers a difference between the temperatures of the two bodies.

We made the experiment with two small identical bulbs; putting in one of them 1 grm. of radiferous barium chloride containing about one-sixth of its weight of radium chloride, and in the other 1 grm. of pure barium chloride. The junctions of the thermo-electric couple were placed in the centre of each cell respectively surrounded by the chloride. The cells were isolated in the air in the centre of two identical vessels, themselves situated in a third which was calorifically isolated, and in which the temperature was practically uniform. Variation in the surrounding temperature under these conditions affects both junctions in the same way, and has no influence on the reading of the couple.

We have by this apparatus proved that there is a difference of temperature of 1·5° C. between the radiferous barium chloride and pure barium chloride, the radiferous salt having the higher temperature. As a check, we repeated the experiment under the same conditions with two cells, both containing pure barium chloride. The differences of temperature observed in this case were only of the order of greatness of $\frac{1}{100}$th of a degree.

We next endeavoured to evaluate the heat evolved by radium in a given time quantitatively.

In order to do this, the heat thus evolved is compared with that evolved by an electric current of known intensity flowing through a wire of known resistance. A bulb containing radium was enclosed in a block of metal, to which it communicated its heat. One of the junctions of the thermo-electric couple was placed in a cavity hollowed out of the metal, the other junction in a second similar block which contained no radium. When contact is established, the block receives from the radium in a given time as much heat as it loses by conduction and by radiation towards the outside. The couple therefore registered a certain difference of temperature between the two blocks.

When the experiment was finished, the bulb containing the radium was removed, and for it substituted a bulb in which was coiled a fine wire of platinum-iridium, which was heated by a current of electricity. The intensity of the current was varied until the difference of temperature between the two blocks was the same as in the preceding experiment. The heat evolved by the radium in the first experiment is thus equal to that evolved in the same time by the current in the second experiment. This latter quantity is easy to calculate.

We have further evaluated the heat evolved by radium by direct measurements with the Bunsen calorimeter.

Before making the experiment, it was first necessary to ascertain that the level of the mercury in the stem of the calorimeter remained absolutely steady. The bulb containing the radium was kept during this time in a tube maintained at zero by melting ice. At a given moment, the bulb was introduced into the calorimeter, and it was found that the mercury in the stem was displaced with a perfectly uniform velocity (2·5 c.m. per hour, for example, with the quantities mentioned above). When the bulb containing the radium was removed, the mercury at once remained stationary. The grm. of radiferous barium chloride with which the majority of these experiments were performed evolved about 14 small calories per hour, but its composition was not exactly known. According to its radio-activity, it should contain about one-sixth of its weight of pure radium chloride. Further experiments were made with a specimen of 0·08 grm. of pure radium chloride. Measurements made by both methods lead to results which are of the same order of greatness without being absolutely concordant.

In our first researches we are proposing only to demonstrate in an indisputable manner the existence of this evolved heat by working under varying conditions and giving the order of greatness of the phenomenon.

One grm. of radium evolves in one hour a quantity of heat which is of the order of 100 small calories per hour.

One grm. atom of radium (225 gr.) evolves during one hour 22,500 calories, a number comparable with that of the heat evolved by the combustion of 1 grm. atom of hydrogen.

The continuous evolution of such a quantity of heat cannot be explained by ordinary chemical transformation. If we look for the origin of the heat in an internal transformation, this transformation must be of a very profound nature, and must be due to a modification of the atom of radium itself. However, such a transformation, if it exists, takes place with extreme slowness. Indeed, the properties of radium show no variation after several years, and Demarçay observed no difference in the spectrum of the same specimen of radium chloride during experiments made at intervals of five months. If therefore the above hypothesis is correct, the energy brought into play during the transformation of the atoms must be extraordinarily great.

The hypothesis of a continuous modification of the atom is not the only one compatible with the evolution of heat by radium. This evolution can also be explained by supposing that radium is capable of utilising an external energy of unknown nature.—*Comptes Rendus*, cxxxvi., p. 673.

AN ATTEMPT TO ESTIMATE THE RELATIVE AMOUNTS OF KRYPTON AND OF XENON IN ATMOSPHERIC AIR.*

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.

WHEN Dr. Travers and I isolated krypton and xenon from air, we had very little idea of the total amount of liquid air from which, by its evaporation, these gases had been obtained. And we were then more concerned with the isolation of the gases in a pure state than in the determination of the proportion in which they exist in the atmosphere. Our knowledge of the composition of the air, however, is not complete until the total yield of krypton, xenon, neon, and helium has been determined. An estimation of the last two is being undertaken by Dr. Travers.

In our experiments on these gases ("Argon and its Companions," *Phil. Trans.*, vol. cxcvii., A, pp. 47—89; abstract in CHEMICAL NEWS, 1900, vol. lxxxii., p. 257) we did not measure the total quantity of air evaporated. We used liquid air for various purposes, and for some months we collected the dregs, allowing them to evaporate into a large gas holder. We guessed (but it was only the roughest estimate) that we had accumulated in this manner the residues from about 30 litres of liquid air; and on this assumption we thought the following estimates not improbable:—Helium, 1—2 parts per million of gaseous air; neon, 1 per 100,000; krypton, 1 per million; xenon, 1 per 20,000,000. But they rested on a very insecure foundation of fact.

The first preliminary experiment was made to ascertain how much of the air which passes through the Hampson liquefier is converted into liquid. The results, however, were inaccurate, and I would rather cite the conclusions given by later experiments on a much larger scale. The compressor was run for several hours every morning and afternoon during six and a half days; the liquefied air was weighed after each run; and the escaping air passed through a large gas-meter, where its volume was registered. The air escaping had a somewhat lower density than ordinary air, owing to the partial removal of

* A Paper read before the Royal Society, March 26, 1903.

oxygen and argon; but the experiments were not sufficiently accurate to make it worth while to take this into account. The volumes given are, however, corrected for alterations of pressure and temperature. In all, 179·7 kilos. of gaseous air passed the meter, and 10·8 kilos. of liquid air were collected. During the collection, about 6 per cent of the liquid air evaporates; adding this, 11·4 kilos. must have been the total weight of air liquefied. The total weight of air taken in by the compressor, therefore, and delivered to the liquefier was consequently 179·7+11·4=191·1 kilos., and the percentage liquefied a little under 6 per cent. The number may be taken without sensible error as 6 per cent liquefaction.

During these runs the pressure was kept at 190 atmospheres; and the delivery of air through the escape valve of the liquefier remained fairly uniform. Separate readings, taken at different times, of the amount of air passing the meter gave 0·244, 0·230, 0·258, 0·261, 0·248, and 0·239 kilos. per minute; these figures testify to fairly uniform working.

It was of interest to see whether argon concentrated itself in the liquefied portion of the air, or whether most of it escaped as gas. The boiling-points of the principal atmospheric gases are on the absolute scale:—Nitrogen, 77·54°; argon, 86·90°; oxygen, 90·5°; the differences are 9·36° and 3·6° respectively; it was therefore to be expected that the argon would concentrate in the liquid.

An experiment was therefore made in which 12·73 grms. of freshly collected liquid air was allowed to boil in a double-walled vacuum tube, and the gases were led directly over metallic copper and magnesium lime; the resulting argon measured 165 c.c. at 0° and 760 m.m. pressure. The weight of this argon was 0·2943 grm., or from 1 grm. of liquid air, 0·02312 grm. Now 1 grm. of atmospheric air contains 0·0129 grm. of argon; hence the process of liquefaction nearly doubles the content of argon in the air. It is, therefore, very advantageous to prepare argon from air which has been liquefied.

Acting on this suggestion, it appeared *à fortiori* probable that if the percentage of argon in air were doubled by liquefaction, the krypton and the xenon would be practically wholly removed and liquefied. And by submitting liquefied air to a second liquefaction, by boiling it off through the compressor, it appeared to hold that a concentration of the krypton and xenon would result, and that they would be found wholly in the liquefied portion. An experiment was therefore begun in which about 100 kilos. of gaseous air were passed through the liquefier; the liquefied portion, amounting to about 6 kilos., was again passed through the liquefier, somewhat added to by gaseous air, drawn in by the compressor. By an unfortunate accident, however, nine-tenths of the air collected during the second liquefaction was lost; and the amount of xenon and krypton in the remaining tenth, representing about 10 kilos. of gaseous air, did not appear to justify repetition of the troublesome experiment. I have no doubt, however, that had these experiments not had for their object the determination of quantity, but only the preparation of krypton and xenon, they would have effected the separation well.

The liquid air, resulting from the liquefaction of 6 per cent of 191·1 kilos. of gaseous air, was sucked, several litres at a time, into a large glass balloon of about 5 litres capacity, fitted with an indiarubber cork, through which a wide tube passed, connected with a double-acting Fluess pump, driven by an electric motor. Through another hole in the cork there passed a syphon which could be closed by means of a brass stopcock; this tube served to admit liquid air to the balloon. A manometer was also connected with the interior of the flask so as to register the pressure under which the liquid air was boiling. The air boiled at a pressure of about 250 m.m., corresponding to a temperature of about −195°. The boiling was quite quiet, without bumping; it was sometimes necessary to warm the balloon gently in order to accelerate the evaporation. The object of distilling at a low temperature was to lower the vapour-pressure of the krypton and xenon in the liquid air, and so to lessen, or in great part to prevent, their evaporation. The total liquid air was thus reduced to about 200 c.c.

The balloon containing this air was coupled with a large iron tube, holding about 20 kilos. of reduced copper heated to bright redness. The liquid air residue, naturally, consisted largely of oxygen, for the more volatile nitrogen had in great part evaporated. After passing over the copper the volume of gas was about 50 litres.

It may be contended that during the evaporation of the air, even at −195°, a large portion of the krypton and xenon may pass away as gas. It is not possible to estimate the amount lost in this manner; but at −195°, the vapour-pressure of krypton is 2·8 m.m., and that of xenon 0·02 m.m. These figures have been arrived at in the following manner:—Relying on the vapour-pressures of mercury by Ramsay and Young, given in the *Trans. Chem. Soc.*, 1886, p. 50, and on the measurements made by Ramsay and Travers (*Phil. Trans.*, 1901, p. 72) of the vapour pressures of krypton and xenon, ratios were found between the absolute temperatures of mercury on the one hand, and of krypton and xenon respectively on the other, between the pressures 300 and 3000 m.m., with two additional data—the temperatures of krypton corresponding to pressures of 9 and of 17·4 m.m. They are as follows:—

Pressures (m m.).	Temp. of mercury. Degrees absolute.	Temp. of krypton. Degrees absolute.	Ratios.	Temp. of xenon. Degrees absolute.	Ratios.
9·0	454·8°	94·2°	0·1851	—	—
300	582·2	110·4	0·1897	148·9°	0·2257
400	596·4	113·8	0·1909	153·2	0·2569
500	609·0	116·1	0·1907	156·8	0·2575
600	617·9	118·35	0·1915	159·7	0·2583
700	626·5	120·2	0·1918	162·0	0·2586
760	631·2	121·3	0·1922	163·9	0·2597
3000	726·8	142·2	0·1957	192·4	0·2647

These ratios were mapped against the absolute temperatures of mercury, and were found, as usual, to give straight lines. The lines were extrapolated to lower temperatures, and the vapour-pressures required were calculated from the extrapolated curves.

The portion of interest is given in the following table:—

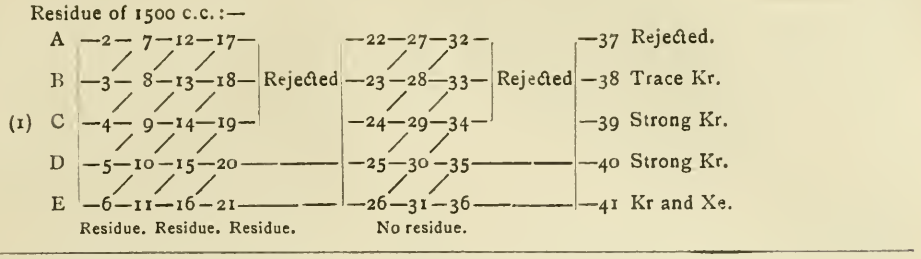
Temperature. °C.	Vapour-pressure of krypton. M.m.	Vapour-pressure of xenon. M.m.
−205	0·27	0·0005
−200	0·97	0·007
−195	2·8	0·02
−190	7·5	0·04
−188·8	9·0	0·11
−182·4	17·4	0·17

The last two data for krypton are the results of direct measurement. It may be mentioned here that the melting-point of krypton is about −169°, and that of xenon −140°; and the boiling-points at atmospheric pressure are—krypton −151·7°, and xenon −109·1°.

The nitrogen was removed from the 50 litres of gas by passing it over red-hot magnesium-lime mixture. The resulting crude argon measured 12·5 litres at 16° and 770 m.m.; its weight is calculated from its known density as 21·3 grms.

This argon was liquefied in a bulb immersed in liquid air, boiling under reduced pressure, so as to reduce the vapour-pressure of the krypton and xenon; and the major part was re-transferred through a Töpler pump to the gas-holder from which it had passed to the liquefying bulb. About 1500 c.c. of the last portions to distil away were collected in five mercury gas-holders, each of a capacity of 300 c.c. The argon was now methodically fractionated according to the accompanying scheme.

The 1200 c.c. numbered (1) was, as described, distributed in five gas-holders. The contents of the first—the one first



filled is termed A—was liquefied, and half the amount replaced in gas-holder A. The contents of B were liquefied, and A was filled, by allowing the liquid argon to evaporate under reduced pressure. The contents of C were liquefied along with what remained of B; and B was filled in like manner. D was liquefied, and C filled; and, finally, E and D filled. The residue in the liquefying bulb, which evaporated very slowly after the argon had boiled away, was removed through the pump, and collected in a tube over mercury. The contents of A, B, C, D, and E are labelled 2, 3, 4, 5, and 6. The process was repeated; and with this explanation the scheme can be understood.

No. 41 was mixed with the residues, which contained much xenon, along with krypton. Nos. 38, 39, and 40 were mixed, and the fractionation continued in a small apparatus. The gases were now sparked with oxygen over soda, so as to remove traces of air; for the operations had now to be conducted with great care, and the spectra of the two samples showed traces of nitrogen. After withdrawal of oxygen from both sets of gas, by means of phosphorus, the krypton mixture was fractionated into three portions; 42, containing much argon; 43, rich in krypton; and 44, a non-volatile residue. The xenon residues, 41, were also solidified with liquid air, and placed for a few seconds in connection with the vacuum of the Töpler pump. The gas which was pumped off was added to 43, and the residue to 44. The bulb was now left for a quarter of an hour, so that equilibrium might be restored, and the stopcock opened a second time. A bubble or two was removed with the pump. On making communication with the pump a third time, no gas escaped; and this is not remarkable, for the vapour pressure of xenon is little over 0·1 m.m. at that temperature. It was therefore assumed that the final residue was pure xenon; and, indeed, its spectrum showed no trace of the krypton lines. And it may also be taken for granted that very little xenon was added to No. 43. The densities of Nos. 42 and 43 were determined; and from the known densities of argon and krypton, their relative proportions were calculated.

The density of 42 was found to be 21·31, corresponding to the percentage composition, argon, 93·5 per cent; krypton, 6·5 per cent; the density of 43 was 39·43, implying a mixture of argon, 6·6 per cent, krypton, 93·4 per cent. The volume of No. 42, reduced to 0° and 760, was 220 c.c.; it therefore contained 1·43 c.c. of krypton; that of No. 43 was 6·5 c.c., and it contained 6·1 c.c. of krypton. The total volume of krypton was therefore 7·5 c.c., and its weight 0·0028 grm.; the volume of the xenon, reduced to 0° and 760 was 0·87 c.c., and its calculated weight 0·0005 grm.

These results are reproduced in the accompanying tabular statement (see next column).

As before remarked, it is not maintained that all the krypton and all the xenon have been separated; it is likely, however, that the separation of the xenon was more perfect than that of the krypton. The results are merely brought forward as the result of a careful experiment to quantitatively isolate these gases.

I have to express my cordial thanks to Mr. E. C. C. Baly and to Mr. Inglis for aid in carrying out part of these operations.

As a quantity of pure krypton, sufficient for determination of density, had been collected, occasion was taken to re-determine the density of that gas. It was submitted to careful fractionation; a considerable portion was rejected as possibly containing argon, and the dregs were set aside as possibly having contained xenon. The substance weighed had a low vapour pressure—about 15 m.m. at the temperature of the liquid air used in fractionating. The separation of the lighter and heavier portions was repeated four times, the density having been determined on each occasion, with only small differences. Finally, a very careful determination of density was carried out, with the following results:—

Volume of density-bulb	7·268 c.c.
Temperature	15·57° C.
Pressure on gas, corrected..	754·0 m.m.
Weight..	0·02488 grm.
Hence density, compared with O=16 ..	40·81

Previous determinations with two samples of gas, one fractionated from argon, the other fractionated from xenon, gave 40·82 and 40·73 respectively as the density. The result given above is in perfect concordance with these figures. The chief cause of error is in the weight; I think it would be fair to regard two units in the fifth place as the limit of error, which gives a possible divergence of about 1 part in 1200.

The atomic weight of krypton would accordingly be 81·62; the mean of former determinations is 81·28. This is in accordance with its position in the periodic table, which lies between bromine, 80, and rubidium, 85.

Air passed through liquefier	191·1 kilogrms.
Air liquefied	11·3 kilogrms. = 5·91 p.c.
Argon obtained (11·8 litres at 0° and 760)	21·3 grms.
Argon per cent of gaseous air	0·0118; of liquid air, 0·1885
Total krypton obtained ..	0·0028 grm.
Total xenon obtained	0·0005 grm.
Percentage krypton in gaseous air	0·000014 by weight
Percentage xenon in gaseous air	0·0000026 by weight

Krypton equal to 1 part by weight in about 7 millions of air; by volume, 1 part in 20 millions.

Xenon equal to 1 part by weight in about 40 millions of air; by volume, 1 part in 170 millions.

Oxygen.—There has recently been placed on the market an oxygen generator which is likely to be a great boon to any having an occasional use of a supply of this gas. The apparatus consists essentially of a metal retort heated by a spirit-lamp, a washing-tank, and a gas-bag. Cylinders of compressed chlorate of potash and manganese are supplied for charging the retort, and the whole apparatus is packed up in a strong iron-bound box. There appears to be nothing that can easily get out of order, and a supply of gas can be obtained in a few minutes and maintained in sufficient quantity to supply an ordinary oxy-hydrogen lantern for any reasonable time. The apparatus is manufactured by the International Oxy-generator Syndicate, Ltd., 21, Southampton Row, W.C.

SOME ADDITIONAL REMARKS ON THE CONNECTION BETWEEN METALS AND NON-METALS, AND ITS BEARING ON THE VALENCE THEORY OF HELMHOLTZ AND ON STEREO-CHEMISTRY.

By GEOFFREY MARTIN, B.Sc.(Lond.).

In a previous paper (Chemical News, 1902, lxxxvi., 295) I suggested that a low temperature would transform metals into non-metals. If this suggestion be correct, some extremely remarkable results follow as a consequence.

1. At some temperature above absolute zero all substances recognised as metals at ordinary temperatures would become almost incapable of conducting electricity. Lord Kelvin believes at the absolute zero that all substances are absolute non-conductors of electricity (*Phil. Mag.*, March, 1902).

2. They would also become incapable of conducting heat, since a capacity for conducting heat in general is associated with a capacity for conducting electricity.

It is natural to infer that at the absolute zero to temperature all substances become absolute non-conductors of heat. This result was arrived at (and communicated to the Physical Society) by Mr. Brinkworth and myself towards the end of 1901 as a consequence of the breach of the law of thermal equilibrium at very low temperatures (*vide* Chemical News, 1902, lxxxv., 194). This and some other equally remarkable results of the reasoning contained in that paper will be published later.

3. At these very low temperatures the bodies recognised as metals at ordinary temperatures would lose their metallic lustre, and become in most cases brightly coloured solids; presenting, in fact, an appearance similar to that presented by the non-metals sulphur or iodine at ordinary temperatures.

It must be remembered the colour of metallic substances is completely hidden by their metallic lustre. Yet most of these metals are undoubtedly very vividly coloured bodies.

For example, the vapour of sodium is violet, just as the vapour of iodine is violet. Silver produces a blue vapour. Gold in thin layers transmits a greenish light. In a solid condition, therefore, and in such a state that the effect of their metallic lustre is eliminated, we should expect such substances to appear quite as brightly coloured as solid iodine or sulphur.

3. Since the valency bonds of a metal are of an electro-positive nature, while the valency bonds of a non-metal are of an electro-negative nature; then, if a metal can be transformed into non-metal by simply lowering the temperature sufficiently, it follows that the difference between a negative and positive valency bond lies not in any absolute difference in the nature of the electrons (atoms of electricity), which are supposed to cause the phenomena of valency (Helmholtz, *Journ. Chem. Soc.*, 1881, xxxix., 277), but solely in the difference in the stability with which the electrons are held by the atom.

If these electrons are very firmly held by the atoms (non-metals) they give rise to what are known as negative valency bonds. If feebly held (metals) they give rise to positive valency bonds.

This conclusion is supported by other considerations.

(*a*). Carbon, a non-metal, is tetravalent, and therefore possesses four negative electrons condensed on its surface. Tin, a metal of the same group, possesses four positive electrons, being also tetravalent.

If these valencies were in the two cases caused by two entirely different-in-nature entities (such as positive and negative electrons are often supposed to be), these two sets of valencies should behave quite differently. But this is not the case.

Tin combines with the same radicles as carbon (*e.g.*, Cl, O, CH_3—, C_2H_5—, &c.), and produces corresponding compounds.

Not only is this so, but tin can actually replace optically active carbon in certain bodies and without the compounds losing their optical properties, as Mr. Pope has shown (*Journ. Chem. Soc.*, 1900).

This last case clearly demonstrates that the tin atom can combine with the same radicles as the carbon atom, and in such a manner that the individual radicles are attached to the tin atom in precisely the same way that they were attached to the carbon atom.

So that the four valencies of the tin atom produce precisely the same effect as the corresponding four valencies of carbon.

It is therefore highly improbable that the valencies of tin are produced by a cause diametrically opposite to that which produces the valencies of carbon, as would be the case were the so-called positive and negative electrons of an entirely different nature.

A similar argument applies to other groups of elements (*e.g.*, the N—Bi group), and to the replacement of H by Cl.

(*b*). The more heavily charged with electrons is an atom the greater the mutual repulsion the electrons exert on each other.

An addition of electrons to an atom, therefore, produces the same effect on the stability with which the electrons are held as an increase of temperature. In both cases the negative valencies should tend to become positive, if the positive or negative nature of a valency bond depends only on the degree of stability with which the electron producing that bond is held by the atom. A great many examples can be quoted showing that this actually does take place. In fact, it is a well known empirical generalisation that unsaturated radicles are electro-negative and saturated radicles usually electro-positive in nature. We quote two of the most striking examples.

Iodine.—The valency bond attached to monovalent iodine is strongly electro-negative (*cf.* KI, AgI, &c.). But when two additional electrons are added to the iodine atom the valencies become strongly electro-positive. For example, the residual valence attached to I in the radicle $C_6H_5>I—$ acts in the same way as the valence attached to the thallous atom, Tl— (V. Meyer, *Ber.*, xxv., 205).

Nitrogen.—The valency bonds attached to trivalent nitrogen are strongly electro-negative. For example, the residual valence in in the system $\overset{H}{H}>N—$ can enter into combination with metals, and play the part of the negative valence of the system HO—, as appears manifest from the large number of metallic amido-compounds now known to exist.

But when we endow the nitrogen atom with three additional electrons (as in the system $\overset{Et}{Et}>N—$), the residual valence changes to sharply positive, the residual valence of the radicle $Et_4N—$ being as strongly electro-positive as that attached to an Na or K atom; $Et_4N—OH$ is, in fact, as powerful a base as NaOH. *We thus arrive at the generalisation that one, and only one, kind of electrons cause the phenomena of chemical valence. The electrons can cause an atom to appear either as electro-positive or electro-negative in nature according as they are feebly or firmly held by the atom.* This places us in a position to define the law of the special arrangement of the valence bonds on the surface of the atom. For electrons, being equally charged particles of like sign, repel each other with the same force.

Therefore in the case of a polyvalent spherical atom whereon several electrons are condensed by the attractive power of the material out of which the atom is composed, the mutual repulsion between the electrons will cause them to take up a position of equilibrium on the surface of the sphere such that each is as far removed as

possible from its neighbour, and if possible in a symmetrical position.

Therefore the manner in which the electrons (and, consequently, valency bonds) distribute themselves over the surface of an atom depends only upon the number of electrons, and not at all upon the nature of the material out of which the atom is composed. The problem, therefore of determining the shape of an atom of valency n is reduced to the problem of distributing n points as symmetrically as possible over the surface of a sphere. We infer—

1. The shape of an atom depends only upon its valency. All atoms which possess the same number n of valency bonds have the same shape, provided that there exists only one way of arranging symmetrically these n points over the surface of a sphere.

2. When the valence of an atom changes, its shape also changes, and in a way that depends not at all upon the nature of the atom, but solely upon the final value of its valence.

We have deduced these generalisations by assuming the atoms on which the electrons are condensed are spherical. Even if this is not so, the same results hold approximately true on account of the very great repulsion that electrons are capable of exerting on each other.

The first of the generalisations is supported by the phenomena of isomorphism (Mitscherlich's law), though of course the result is only strictly true when all the atoms or radicles attached to the central atom are identical, and attract each other with a force *much less* than the repulsive force which exists between the electrons by which they are attached to the surface of the central atom.

The second generalisation has, in a less general form, been already enunciated by Mr. Pope as a result of his experimental researches (*Journ. Chem. Soc.*, 1900, lxxix., 828).

Kiel, March, 1903.

ORIGIN OF THE WORD "BAROMETER."*

By H. CARRINGTON BOLTON.

THE instrument familiar to us all as the barometer was first universally known by the name of its inventor as "Torricelli's tube"; de Guericke, the inventor of the air-pump, called his huge water-barometer "Semper Vivum," also "Weather Mannikin," with the Latin form "Anemoscopium.

Soon after the year 1665 the words "baroscope" and "barometer" came into general use in England, but the individual to whom the credit belongs for originating these terms has not been certainly known; the assertion made by a contributor to the *Edinburgh Review* for 1812 that "baroscope" was first used by Prof. George Sinclair, of Scotland, in 1668, is an error, for both words occur in the *Philosophical Transactions* four years earlier. The passage is unsigned, and reads thus:—

"Modern Philosophers, to avoid Circumlocutions call that Instrument, wherein a Cylinder of Quicksilver, of between 28 and 31 inches in Altitude, is kept suspended after the manner of the Torricellian Experiment, a Barometer or Baroscope, first made Publick by that Noble Searcher of Nature, Mr. Boyle, and imployed by him and others to detect all the minut variations in the Pressure and Weight of the Air."

The mention of the words in connection with the name of Robert Boyle has led me to make a close examination of his voluminous and prolix writings. In Boyle's first publication, "New Experiments Physico-Mechanical touching the Spring and Weight of the Air," dated 1660, the words baroscope and barometer do not occur; he uses the common term "tube," and often writes of the "mercurial cylinder." Nor are these words used by him in his "Defense of the Doctrine touching the Spring and the Weight of the Air . . . against the objections of Franciscus Linus," a paper published in 1662.

Their use by the anonymous writer to the *Philosophical Transactions* in 1665 has been shown, and the question arises who was this person who modestly concealed his name; I believe it was Boyle himself. This eminent man, who was so devoid of personal ambition that he declined a peerage, had a habit of writing about himself and his scientific labours in the third person, and often spoke of himself by fanciful fictitious names, such as "Philaretus" (in his fragmentary autobiography) and "Carneades" (in the "Sceptical Chymist"). That he should send an unsigned communication to a journal was not surprising, particularly as he had occasion to mention himself.

Be this as it may, my claim that Boyle originated the word barometer does not rest on such slender conjectures as these. One year later than the communication in the *Philosophical Transactions*, Boyle wrote to this journal (dated April 2, 1666) and says:—"Barometrical observations (as for brevity's sake I call them)," using the personal pronoun this time. Elsewhere in the same paper are found the terms barometer, baroscope, and baroscopical observations.

In his "Continuation of New Experiments Physico-Mechanical . . ." of which the preface is dated 1667, occurs the following phrase:—"But though about the barometer (as others have by their imitation allowed me to call the instrument mentioned)," (Boyle's Works, Birch's Edition, Vol. III., p. 219, London, 1744).

This sentence is virtually an admission by Boyle that he had coined the word, since others imitating him had allowed and encouraged him to use the term to designate the tube of Torricelli.

I conclude, therefore, that the word "barometer" was introduced into our language by the English philosopher, the Hon. Robert Boyle, about the year 1665. Boyle, by the way, was a scholar and able to use Greek in forming an English word. Finally, I may add that examination of Murray's, Skeats', and other standard English dictionaries throws no light on the origin of the word; they merely refer to the *Philosophical Transactions*, and give its obvious etymology.

* Advance proof from *Science*.

ON THE GRAVIMETRIC ESTIMATION OF TELLURIUM.

PART II.

By R. W. EMERSON MACIVOR, F.I.C., &c.,
Formerly Assistant Professor of Chemistry, Anderson's College (Medical Faculty), Glasgow.

IN this communication I propose to deal with the merits or otherwise of several gravimetric processes for estimating tellurium which were not discussed in my previous paper (CHEMICAL NEWS, vol. lxxxvii., p. 17), and also to notice some peculiarities of the precipitated so-called element which I think are likely to have special interest for analytical chemists.

Stannous chloride was employed by the earlier chemists, and is still recommended in some of our principal text-books as a precipitant of tellurium from tellurous solutions, and although known to be so efficient that by its aid one part of the element in 70,000 parts of solution can be detected, it is found in quantitative work that the precipitate thrown down by it is never pure, but always contains a variable quantity of tin which cannot, without very considerable trouble and loss of time, be separated or allowed for, and therefore interferes more or less seriously with the accuracy of the final result. On this ground alone I am unable to endorse the favourable opinion expressed by some authorities regarding the $SnCl_2$ method of precipitation.

Donath states (*Zeit. Ang. Chem.*, 1890, p. 214—217) that in his opinion hyposulphurous acid is a good reducing agent for TeO_2 in cold concentrated acid solutions, and that the precipitating liquid may be easily prepared by digesting metallic zinc in an aqueous solution of SO_2. It is asserted that when this liquid is mixed in some excess with the tellurous solution, complete precipitation takes place in about fifteen minutes. On testing the process, I found, however, that a perfect separation of tellurium cannot be brought about in the cold, and, even if this were possible of attainment, the precipitate produced is in nature so finely divided that its collection and after treatment is tedious work. But if the mixed solution is heated to boiling-point for a sufficient length of time—and this will vary according to circumstances—the whole of the tellurium will ultimately come down in a form in which it can be easily manipulated as far as the merely mechanical process of washing and filtering are concerned; on the other hand, the precipitate contains an admixture of sulphur, which is not constant in amount, and which can only be removed by extraction with CS_2, or by prolonged heating in a stream of inert gas at a temperature of 250° or so, whereby the sulphur is vaporised and carried off. Oxidation with HNO_3 in a porcelain crucible and subsequent gradual heating to over 400° has been suggested as a simpler method of dealing with this unsatisfactory precipitate, but I have found that before the last traces of acid can be expelled from the TeO_2 formed, a not inconsiderable quantity of the latter also volatilises. In view of these facts I fail to see that Donath's method can in any sense be considered an advantageous substitute for the ordinary sulphite process.

I now come to speak of the grape or invert sugar reduction process devised by Stolba thirty years ago (*Jahr. f. Chem.*, 1873, 214), and approved by Kastner (*Zeit. Anal. Chem.*, 1875, 142), and in later years by other workers. It has much to recommend it on the score of simplicity, ease of execution, and reliability. It is necessary that the tellurous solution to be precipitated after neutralisation with Na_2CO_3 (in some excess) should be heated to boiling for a few minutes before the sugar solution is mixed with it, and this should be done in considerable excess, so that perfect precipitation may be effected and the oxidation of the tellurium prevented; the mixed solution should be boiled for about twenty minutes, rarely longer. In the condition in which it comes down the precipitate can be washed by decantation (which should be done over and over again with hot water), and afterwards on the filter with, first, water, and afterwards repeatedly with alcohol; it shows less tendency to absorb oxygen—or at least appeared to me to do so—than the tellurium thrown down in acid solution. I find the Stolba process a convenient one in the analysis of telluriferous minerals. The material, in a finely ground state, should be digested for a time—an hour is usually long enough even in the case of an obstinate mineral—in strong HNO_3, the mass then evaporated to almost dryness over the water-bath, and the residue boiled for thirty minutes or so in a strong solution of NaOH. Water is next added, and the hot solution filtered, some HCl is next added to the filtrate in order to destroy its excessive alkalinity, and the liquid evaporated to small volume. To this still alkaline solution an excess of the sugar solution is now added, and the whole boiled for about twenty minutes, when precipitation should be complete. The precipitate should be collected and treated in the manner just explained.

The powerful deoxidising properties of hydrazine hydrate and its hydrochloride have recently been applied by Gutbier (*Ber.*, 1901, [12], 2724—2726) to the quantitative precipitation of tellurium from both telluric and tellurous solutions. To acid solutions either of these compounds may be added, but in the case of an alkaline solution it is advised that the hydrochloride should be used. In his paper the inventor confines the description of his method of working the process to the reduction of telluric acid solutions, and leaves the reader to adapt it as he may think best to other tellurium compounds. To the warm telluric solution, contained in a capacious porcelain (or platinum) dish provided with a spout, and also with a glass (or platinum) cover, a 10—20 per cent solution of either $N_2H_4H_2O$ or the hydrochloride is added by aid of a pipette inserted in the spout, the dish being meanwhile kept well covered to prevent loss by spirting. The reduction at once commences, being indicated by the liquid becoming dark blue or nearly black, and after heating to 100° for a few minutes the solution clears again while the tellurium separates in a flocculent condition. Successive additions of the reducing agent are made until it ceases to cause colouration, and when this point is reached the whole of the tellurium will have separated from the solution. The precipitation is much facilitated by heating the solution after each addition of the precipitant, and the supernatant liquid should be passed through the tared filter upon which the bulk precipitate is ultimately put, after having been thoroughly washed (by decantation) with hot water containing a little $N_2H_4H_2O$ to prevent oxidation. I cannot pretend to have had much experience with the Gutbier process, nor am I now likely to have for some time to come, but so far as my few trials of it can guide me to an opinion, I am disposed to believe it has advantages not possessed by certain other methods—even the sulphite process. The point of complete precipitation is easily struck, since a fresh addition of the reagent will no longer impart a colour to the solution; the precipitate separates quickly and in excellent condition for after treatment, and its oxidation is reduced to a minimum.

Properties of Tellurium Precipitates.

If there is a substance of all others which demands that the solutions from which it is to be precipitated should be as concentrated as possible before the precipitating agent is mixed with them, it is surely tellurium. From dilute solutions it is not only very difficult to obtain the perfect separation of the element, but the form in which it is precipitated renders its collection and general management most wearisome and unsatisfactory. Tellurium should, whenever possible, be thrown down from hot or boiling solutions, and the heating should be continued (always in the presence of an excess of the reducing agent) until the precipitate has so aggregated that it settles well and can be filtered and washed with facility. "It is to be noted," says Crane, who has had a long experience of the subject, "that differences in the concentration (and temperature) of the tellurium solution in which the precipitation takes place may markedly influence the character of the precipitate." Only those who have had much to do with tellurium precipitates can appreciate to the full the truth of these few words.

It has been shown that precipitated tellurium is with difficulty freed from the acids it may bring down with it from solution, particularly H_2SO_4 and HCl. Thus Brauner (*Journ. Chem. Soc.*, vol. lv) found a precipitate (produced by SO_2 in an acid solution of TeO_2) which had been most carefully washed first with water and then with alcohol, and dried at 110°, still retained appreciable quantities of these two acids, and on being heated to 300° in a current of hydrogen gave off vapours which, when passed into a solution of $AgNO_3$, caused a white precipitate of AgCl, and experienced a loss in weight equivalent to 0·31 per cent. This quantity may not at first sight appear important, but when we take into consideration that at the time Brauner made this experiment he was engaged in a most painstaking original research, which, of course, demanded that all his operations should be conducted with an attention to detail and exactitude of manipulation not bestowable on every-day analytical work, the seemingly small quantity of acid impurity which he found in his precipitate has some significance, inasmuch as it indicates the probability of a precipitate similarly obtained and handled in an ordinary laboratory fashion containing an amount of either, or both, of the

acids named which cannot by any means be considered negligible. To remove this impurity, or at least to bring it within a reasonable limit of error, the precipitate should, after a first weighing, be exposed for some time to a temperature of 250—300° in a current of inert gas, say dry CO_2, and again weighed; or it may be digested for a few minutes in hot water containing a little NH_3, again filtered, washed, and dried at 105°. By the latter means I succeeded in extracting from a precipitate which had previously been well washed by decantation and in the filter, 0·198 and 0·397 per cent of HCl and H_2SO_4 respectively. The final weight of this precipitate, I may mention, was 1·6958 grm.

With regard to the absorption of oxygen by tellurium precipitates while still in the solutions in which they were formed and during the processes of washing and drying, I have already said a good deal (Chemical News, vol. lxxxvii., 17), but it is desirable that I should here further refer to it. The extent to which this process will occur while the tellurium remains in contact with the acid liquid will, of course, much depend on circumstances, but, according to Norris and Fay (*Am. Chem. Journ.*, xx., p. 278), the quantity of precipitate which undergoes oxidation in the case of the ordinary sulphite process and which remains behind in the solution as tetrachloride, is, under ordinary conditions of analysis, about 0·5 per cent, and these authorities look upon this loss as being compensated for by a corresponding increase in weight of the precipitate due to the absorption of oxygen during the operations of washing and drying. Thus it is argued that the result obtained by the sulphite process is "approximately true." I have, however, found that a tellurium precipitate weighing 2·5893 grms. increased in weight to the extent of over 2 per cent during six hours' drying at 105°, and this could only arise from the absorption of oxygen. The same precipitate, after being freed from TeO_2 and dried in CO_2 at 110°, was left in the dry atmosphere of a balance case for four months without undergoing the slightest oxidation. Crane suggests (*Am. Chem. Journ.*, xxiii., p. 419) that though the oxidation of the precipitated element is obviously influenced by circumstances, it need not at all seriously affect the final result; it can not only be very easily detected, but its actual extent can be accurately judged. By removing the precipitate from the filter, after it has been weighed, and putting it in a beaker on a white surface or in a white (porcelain) dish and moistening it with strong HCl, any TeO_2 present dissolves, and imparts to the acid the characteristic yellow tint of $TeCl_4$, leaving the unoxidised element untouched, it being absolutely insoluble. The tint should appear immediately the HCl comes in contact with the substance; if, however, it is not then perceptible and only becomes so after some time, it will be due to the oxidation of the tellurium by the air after the addition of the HCl, and not to TeO_2 in the precipitate before this addition was made. With the object of determining how far this colour of $TeCl_4$ could be utilised "as a criterion of the presence of TeO_2 and its amount," Crane dissolved 0·0068 grm. of $TeCl_4$ in HCl, and, on gradually diluting the solution with water, found that the yellow tint of a layer 0 25 cm. "thick" was clearly distinguishable when only 0·00013 grm. of the tetrachloride was present in each c.c.

To prevent, or at least minimise, the oxidation of tellurium precipitates, it is necessary that they should be rendered quite free from the acids mentioned above, as the presence of these appears to assist the process, and in filtering off they should be kept as well covered with liquid as possible so as to exclude air; it is sometimes well, also, to finally wash with pure alcohol. Whenever possible, the Gooch system of filtration should be adopted.

Condensation of the Nitrated Derivatives of Chloride of Benzyl with the Naphthylamines.—MM. G. Darier and E. Mannassewitch, in a very long paper, describe the preparation of a number of colouring matters; they are all very slightly affected by acids and alkalis.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., Nos. 20—21.

THE LECITHANS: THEIR FUNCTION IN THE LIFE OF THE CELL.*

By WALDEMAR KOCH.

(Concluded from p. 150).

Preparation and Analyses of Various Lecithans.

Egg Lecithin.—The yolks of ten eggs are allowed to stand with 600 c.c. ether over night, 1 litre alcohol added, the solution filtered and evaporated on water-bath. The residue is dissolved in 200 c.c. cold ether, and 1 litre acetone added. The precipitated lecithin is treated over night with 1 litre cold alcohol, the solution filtered and evaporated. The residue is once more dissolved in ether, precipitated with acetone, and dried over sulphuric acid in a vacuum desiccator.

I.† 0·8113 g. of the substance gave 0·1136 g. $Mg_2P_2O_7$, *i.e.*, 3·91 per cent P.

II. 0·9150 g. of the substance gave 0·1278 g. $Mg_2P_2O_7$, *i.e.*, 3·90 per cent P.

III. 0·330 g. of the substance gave 0·3001 g. AgI, *i.e.*, 5·80 per cent CH_3.

IV. 0·325 g. of the substance gave 0·2960 g. AgI, *i.e.*, 5·81 per cent CH_3.

V. 0·320 g. of the substance gave, below 240° C., 0·0760 g. AgI, *i.e.*, 153 per cent CH_3. The methyl iodide given off above that temperature was lost on account of an accident. In III. and IV. the methyl iodide came over at 220° C. and 300° C. The two portions were not separated.

		Found.		
		III.	IV.	V.
Phosphorus as 3·97 calculated for $3CH_3$	5·66	5·80	5·81	—
Phosphorus as 3·97 calculated for $1CH_3$	1·88	—	—	1·53

Brain Lecithin and Kephalin.—One kilo. sheep's brains is minced in a meat-chopper, and freed from water and extractives by boiling with 1 kilo. acetone for eight hours. The solution is filtered cold, and the remaining acetone removed from the brains by gentle heating at 50° C. Seven hundred c.c. cold ether are now added and allowed to stand for three days, the solution is filtered, and another portion of ether added, and again allowed to stand. The ether filtrates are united and slowly evaporated to one-fourth their original volume in a tall beaker. The solution is then carefully removed by means of a pipette from the white precipitate, which has settled to the bottom, and 1·5 kilo. alcohol is added to the solution.

Kephalin.—The precipitated kephalin is extracted five times with boiling alcohol, dissolved in ether, precipitated with acetone, again dissolved in ether, and allowed to settle in a long, narrow, closed test-tube. The clear ether solution is removed by decantation, evaporated, and the residue re-crystallised twice from hot acetic ether. The resulting kephalin is very hygroscopic, and must be dried over sulphuric acid for analysis. It agrees perfectly in all its properties with the kephalin described by Thudichum (p. 127). On analysis it gave the following results:—

I. 0·2469 g. of the substance gave 0·5388 g. CO_2 and 0·2159 g. H_2O, *i.e.*, 59·5 per cent C. and 9·7 per cent H.

II. 0 415 g. of the substance neutralised 5·2 c.c. *n*/10 acid, *i.e.*, 1·78 per cent N.

III. 0·9644 g. of the substance gave 0·1330 g. $Mg_2P_2O_7$, *i.e.*, 3·85 per cent P.

IV. 0·7235 g. of the substance gave 0·0990 g. $Mg_2P_2O_7$, *i.e.*, 3·82 per cent P.

V. 0·3488 g. of the substance gave, below 240° C., 0·0945 g. AgI, *i.e.*, 1·73 per cent CH_3.

* From the *Decennial Publications of the University of Chicago*, 1902, vol x.

† For phosphorus determinations the very excellent method of Neumann was used (Engelmann's "Archiv. für Physiologie," 1900, p. 159).

VI. 0·490 g. of the substance gave, below 240° C., 0·1312 g. AgI, *i.e*, 171 per cent CH_3.

VII. 0 225 g. of the substance gave, below 300° C., 0·0636 g. AgI, *i.e.*, 1·80 per cent CH_3.

VIII. 0·748 g. of the substance was burned with a mixture of nitric and sulphuric acid, the solution diluted, neutralised with 50 g. barium hydrate to remove sulphates and phosphates, the barium removed with sulphuric acid, and the solution evaporated. The ignited residue weighed 0·030 g. Some of this must have come as an impurity from the barium hydrate. In any case, the amount is not sufficient to account for any more than an impurity. Thudichum (*op. cit.*, p. 130) has also found his kephalin to contain small amounts of inorganic substances as impurities. My analyses agree fairly well with Thudichum's (p. 132).

Thudichum :—C, 60·0; H, 9·38; N, 1·68; P, 4·27.
My results :—C, 59 5; H, 9·7; N, 1·78; P, 3·84.

The methyl groups correspond very closely to one methyl for one nitrogen. That this is not due to the presence of lecithin as an impurity is shown by the fact that the methyl is all split off below 240° C.

		Found.			
		II.	V.	VI.	VII.
Phosphorus as 3·83 calculated for $1CH_3$ ..	1·85	—	1·73	1·71	1·81
Phosphorus as 3·83 calculated for 1N.. ..	1·73	1·78	—	—	—

Lecithin.—The original alcohol-ether filtrate from which the kephalin has been removed by filtration is evaporated to dryness, and the residue dissolved in ether and freed from cholesterin by precipitation with acetone. The precipitated lecithin is treated with a large quantity of cold alcohol for some time, and the solution filtered and evaporated. The resulting lecithin should dissolve readily and completely in cold alcohol or ether. If this is not the case, the extraction with cold alcohol must be repeated. Finally, the lecithin is dissolved in hot acetic ether, and allowed to separate out by cooling, dried over sulphuric acid, and analysed.

I. 0·2420 g. of the substance gave 0·5683 g. CO_2 and 0·2420 g. H_2O, *i.e.*, 64·04 per cent C; 10·4 H.

II. 0 942 g. of the substance neutralised 12·1 c.c. *n*/10 acid, *i.e* , 1·8 per cent N.

III. 0 677 g. of the substance gave 0·0919 g. $Mg_2P_2O_7$, *i.e.*, 3·79 per cent P.

IV. 0·815 g. of the substance gave 0·1109 g. $Mg_2P_2O_7$, *i.e.*, 3 80 per cent P.

V. 0·3975 g. of the substance gave 0·3156 g. AgI, *i.e.*, 5·1 per cent CH_3.

VI. 0·235 g. of the substance gave 0·1853 g. AgI, *i.e.*, 5·03 per cent CH_3.

My lecithin agrees fairly well in its properties with the one isolated by Thudichum (p. 116). The results of the methyl-group determination show as good an agreement with the theory as can be expected from a compound so difficult to purify.

		Found.		
		III.	V.	VI.
Phosphorus as 3·8 calculated for $3CH_3$	5·51	—	5·1	5·03
Phosphorus as 3·8 calculated for 1N	1·72	1·8	—	—

Lecithans from Yeast.—Twenty yeast cakes are mixed well with 1 litre of alcohol in a flask and boiled for eight hours, filtered, the yeast allowed to stand with ether over night, filtered, the filtrates united, and evaporated. The residue is extracted with cold ether, three times the volume of acetone added, and the resulting precipitate dried *in vacuo* over sulphuric acid, as it is not sufficient for further purification. The substance thus obtained resembles kephalin in that it darkens rapidly on exposure to the air, and is precipitated from ether solution by alcohol. The analysis gave the following result :—

I. 0·220 g. of the substance gave 0·0286 g. $Mg_2P_2O_7$, *i.e.*, 3 63 per cent P.

II. 0·165 g. of the substance gave 0·0626 g. AgI, *i.e.*, 2·42 per cent CH_3.

The methyl iodide was split up mostly at 240° C., but some more was obtained on raising the temperature to 300° C.

		Found. II.
Phosphorus as 3·63 calculated for $1CH_3$	1·76	2·42
Phosphorus as 3·63 calculated for $2CH_3$	3·51	—

The amount of methyl is not sufficient to account for two groups, and as the compound was not especially freed from lecithin, it seems reasonable to account for the extra methyl as due to an impurity of lecithin which would amount to about 11 per cent. The main bulk of the body is, therefore, kephalin, which agrees well with the other observations.

The results so far obtained with the Herzig and Meyer methyl group determine, then, that the two principal classes of lecithans differ, not only in the fatty acid group, but also in the complex which contains the nitrogen. Very striking is the fact that kephalin occurs only in living cells, such as the nerve or yeast cell, and is not found in the egg, which consist mostly of stored food material. Kephalin may possibly be an intermediary product in the decomposition of lecithin. The low amount of carbon and the correspondingly large amount of oxygen would indicate an addition of oxygen in the oleic-acid radical of the lecithin—a hypothesis which leaves unexplained the fact that kephalin is, if anything, more unsaturated than lecithin, judging by the relative amounts of iodine absorbed. At any rate, there is at present not enough known about the nature of kephalinic acid to trace its origin to oleic acid. As far as the nitrogen complex is concerned, it is possible that two methyl groups have been split off, leaving a mono-methyl oxæthylamin. Thudichum (*op. cit.*, p. 147) has, indeed, isolated from his kephalin a base which contains less methyl groups, but he has also mentioned the presence of neurin. My results, however, show conclusively that neurin can be present only as an impurity. The decomposition of 20 grms. of kephalin with barium hydrate yielded only 0·2 g. of a platinum salt, which corresponded, on analysis, to something between a mono- or a di-methyl oxæthylamin. The investigation of this interesting relation will be continued, and the methyl-group determination described above will undoubtedly be of value in following out the quantitative relation of lecithin to kephalin under various conditions in the living cell. The other lecithans, such as the myelins, paramyelins, and amidomyelins, isolated by Thudichum from brain tissues, do not seem to occur in any large quantity, and have not as yet been investigated.

Physiological Properties.

Substances of such importance to the cell as the lecithans must possess some value as foods. The action of the digestive ferments is therefore of especial importance, as neurin, which is formed by the decomposition, has been shown by Halliburton (*op. cit.*, p. 55) to have a decided effect on blood pressure. A. Bókay (Hoppe Seyler's *Zeit. für Phys. Chem.*, 1877, vol. i., p. 157), under the direction of Hoppe Seyler, investigated this problem and found that lipase will split egg lecithin into glycerophosphoric acid, fatty acids, and neurin. The three splitting products must, however, be immediately absorbed and re synthesised, as they are not found in the urine or fæces, and a meal containing considerable lecithin has never been known to cause any bad effects. The results on the metabolism of the injection of lecithin into the circulation are as yet in too unsatisfactory a state to be discussed. The patenting (C. Zerbe, *Chemiker-*

Zeitung, 1902, vol. xxvi., p. 17; Deutsches Reichs-Patent, 127357) of brain preparations for medical purposes seems, therefore, especially premature.

For completeness sake a number of facts have been mentioned in this paper which have been known for a long time. The new facts are as follows:—

1. The word "lecithan" is to be used as a group name, including such compounds as egg lecithin, brain lecithin, kephalin, myelin, paramyelin, &c.

2. The emulsion formed by the lecithans may be the substratum in which the reactions of the cell take place. The precipitation of this emulsion by divalent kations is prevented by univalent and trivalent kations, as far as investigated, and this observation may furnish an explanation of the changes brought about by electrolytes in the living cell.

3. Kephalin is found only in the living cell, and may be an intermediary product in the metabolism of lecithin.

4. An accurate method for determining lecithin and kephalin quantitatively.

NOTICES OF BOOKS.

Analytical Chemistry. By F. P. Treadwell. Translated (with the Author's permission) from the Second German Edition by William T. Hall. Volume I. "Qualitative Analysis." New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. Pp. xi.—466. 8vo.

This book reproduces in a somewhat amplified form the author's lecture to students at the Polytechnic Institute of Zürich. It is designed for laboratory use as well as for "self study," as the translation of the preface puts it, and it contains much information usually found in text-books of general chemistry and of mineralogy. With each element, besides the analytical reactions, the mineralogical occurrence, crystalline form, and isomorphous relations are briefly mentioned; these include many details of descriptive mineralogy. The reactions of the metals forming distinct groups are followed by methods of separation given in schematic tables. Under reactions of the metalloids (anions) those of the acids are given. Part II. is devoted to the systematic course of analysis, and in a Supplement are reactions of some of the rarer metals, arranged in their natural groups.

The introduction has chapters on the Law of Chemical Mass Action, the Ion Theory of Arrhenius, Hydrolysis and Determination of the Sensitiveness of Reagents, a subject on which the author lays much weight (see preface). The section dealing with the reactions of sodium peroxide is followed by one on the reactions of hydrogen peroxide. The method of spectrum analysis is briefly explained in five pages.

A feature of this book is the unusual number of equations explanatory of reactions that are scattered throughout its pages. The author's fondness for representing these reactions by structural formulæ caused them to occupy much space, as seen on pages 100, 117, and 149.

Novelties are rather seldom introduced, but tried methods are given places in the volume, such as Gutzeit's test for arsenic, Griess's test for nitrous acid, and Hillebrand's method for detecting vanadium in rocks. Some of the typographical errors are peculiar; "Bunsen and Kirschhoff" occurs twice, though there is little in churchyards to suggest cherries. The translator has made an attempt to correct the mis-spelling of Kirchhoff in the Supplement, but in vain; it is there given as "Kirchoff"! "Sodium santhogenate" (p. 174) looks unfamiliar, and "tantallium" in the table of contents is supposed to refer to tantalum, which is correctly spelt in the text. This table, by the way, does not correspond accurately with the sections in the volume, especially between pages 19 and 35.

Historical details are rather unequally inserted; the names associated with the discovery of uranium are mentioned, but under neo-dymium and praseo-dymium, no chemist receives credit for his labours on these elements, and under thallium there is no reference to Crookes. The index at the end of the volume is inadequate and rather carelessly made, but these blemishes do not materially detract from the value of the work for the purpose for which it was written. H.C.B.

Chemical Technology, or Chemistry in its Applications to Arts and Manufactures. With which is Incorporated Richardson and Watts' "Chemical Technology." Vol. IV. Edited by W. J. Dibdin, F.I.C., F.C.S., &c. London: J. and A. Churchill. 1903. Pp. 378.

This volume is divided into two distinct portions; the first two hundred and seventy-seven pages are on "Electric Lighting," written by Mr. A. G. Cooke, M.A., &c., and the remainder of the book, comprising one hundred pages, is on "Photometry," and is written by Mr. W. J. Dibdin, who is also the editor of the whole.

We may describe this work as an eminently practical one, though theoretical considerations are by no means neglected, but have indeed several important sections devoted to their study.

The author begins with a short general survey of the functions of what we may call "heavy" electric currents, and then proceeds to the subject of conductors and their accessories.

The different forms of dynamo are dealt with next, both theoretically and practically; this is followed by sections on storage batteries, transformers, and series distribution. We then come to the theory and practice of alternating currents, sections on incandescent and arc lamps; and finally there is a section on "Central Station Economy," which deals with such important items as fuel, boilers, efficiency of machinery and distribution, meters, and methods of charging for electrical energy.

Photometry is a subject very closely allied with the production and distribution of electric light. The laws governing photometry are at first sight extremely simple, the principal one being the law of inverse squares. In practice, however, the subject is surrounded with a number of small difficulties, the chief one being the production of a trustworthy standard of light. The candle has the merit of simplicity and portability, but it is not to be relied upon to the same extent as the more modern lamps, such as Harcourt's pentane flame, and similar substitutes, a number of which are fully described in pages 336 to 353. There are also a number of photometers described; they are naturally all based on the same principle, and are known by the various names of their designers. The book is well written and planned, and will undoubtedly be of service to electrical engineers and others connected with, or interested in, the subjects dealt with.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 10, March 9, 1903.

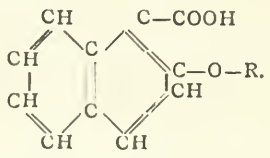
Preparation and Properties of Rubidium and Cæsium Hydrides.—Henri Moissan.—The author finds that rubidium and cæsium unite directly with hydrogen, giving crystalline compounds having formulæ RbH and CsH. These substances are very energetic reducing agents, decomposing water, hydrogen sulphide, and hydrochloric acid at ordinary temperatures. With sulphurous acid at a low temperature they give hydro-

sulphites,; with carbonic acid, and by direct union of the formates with ammonia, amides are formed. These researches complete the author's proof that all the alkaline metals give with hydrogen definite binary compounds, which are crystalline and have the formula RH.

Electric Non-conductivity of Metallic Hydrides.—Henri Moissan.—The author examines the electric conductivity of metallic hydrides, and finds that hydrogen is not comparable in this property with the metals; also that the metallic hydrides are not in any way akin to alloys in chemical or electrical properties. The liquefaction of hydrogen by Professor Dewar confirms the fact that it is more allied to oxygen or nitrogen than to mercury, cæsium, or gallium. Also liquid hydrogen, in the same way as the metallic hydrides, is a non-conductor of electricity.

Cuprous Sulphate.—A. Joannis.—In a previous paper the author described a compound of carbonic oxide and cuprous sulphate in solution which has the curious property of dissociating and giving cupric sulphate and particles of metallic copper on the surface of the solution. This substance, which apparently has the formula $SO_4Cu_2,2CO,H_2O$, decomposes in a vacuum, whether solid or dissolved, and the present experiments seem to show that cuprous sulphate cannot exist in the free state.

Certain Derivatives of Oxy-2 naphthoic-1 Acid.—F. Bodroux.—When bromo-1-naphthol-2 acts on alcoholic iodides in presence of potash, the acid produced evidently has the constitution—



MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, after Easter:—Prof. Allan Macfadyen, three lectures on "The Blood and some of its Problems"; Prof. G. H. Darwin, two lectures on "The Astronomical Influence of the Tides" (The Tyndall Lectures); Prof. E. J. Garwood, two lectures on "The Work of Ice as a Geological Agent"; Prof. Dewar, three lectures on "Hydrogen: Gaseous, Liquid, and Solid"; Prof. S. H. Vines, two lectures on "Proteid-Digestion in Plants"; Prof. J. A. Fleming, two lectures on "Electric Resonance and Wireless Telegraphy"; Prof. Langton Douglas, two lectures on "The Early Art of Siena"; Hamish MacCunn, Esq., two lectures on "Music" (with Musical Illustrations); and Prof. Silvanus P. Thompson, two lectures on "The De Magnete and its Author, (1) The Book, (2) The Man." The Friday Evening Meetings will be resumed on April 24th, when a Discourse will be given by the Hon. R. J. Strutt on "Some Recent Investigations on Electrical Conduction"; succeeding Discourses will probably be given by Prof. William J. Pope, Mr. Rider Haggard, Dr. D. H. Scott, Dr. J. A. H. Murray, His Serene Highness Albert Prince of Monaco, and other gentlemen.

Science in the Provinces.—The recent development of scientific teaching in Ireland has led to the formation in Cork of a new society for the cultivation of science and the promotion of its application to industry. The society has been named the Cork Scientific Association, and its Officers are:—President, Wm. B. Harrington, F.C.S.; Vice-Presidents, Rev. Br. D. J. Burke, Prof. Corby, M.D., G. Fletcher, Dept. Ag. and Tech. Ind., Prof. Marcus M. Hartog, M.A., D Sc.; Hon. Secs., H. G. W. Adan, B.Sc., T. Farrington, M.A., F.I.C., F.C.S., and A. Coulthard, B.Sc.; Hon. Treas., Jas. Comerton, B.A. Three of the monthly meetings have already been held, at which the following papers have been read and discussed:—"On Science Teaching in Irish Schools," by Rev. Br. Crehan; "On a Proposed New Method for Ascertaining the Genuineness of Milk," by T. Farrington, M.A., F.I.C., F.C.S.; "On the Nature of Flame and the Cause of Luminosity," by A. Coulthard, B.Sc. At the next meeting, to be held on Monday, April 20th, Prof. Marcus M. Hartog, M.A., D.Sc., will read a paper on "Ferments," and the Session will close in the following month with a lecture by Mr. G. Fletcher on "Glacier Motion." The Society's activity does not, however, terminate with the close of its Session, as arrangements have been made by which its members are kept in touch with the advance of Science through the circulation of the leading scientific journals all the year round.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "The Manufacture of Iodine from Nitrate Liquors," by Dr. W. Newton, F.I.C., &c. "New Modification of Coffignier's Prussian Blue Reaction, and a Possible Application," by Watson Smith, F.I.C., &c. "The Explosion of Potassium Chlorate at St. Helens," by Dr. A. Dupré, F.R.S.

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THE CHEMICAL NEWS.

Vol. LXXXVII., No. 2263.

A RE-DETERMINATION OF THE ATOMIC WEIGHT OF LANTHANUM.*

By HARRY C. JONES.

A number of determinations of the atomic weight of lanthanum have already been made. The more important and reliable are the following:—

Rammelsberg (*Pogg. Ann.*, 1842, lv., 66) precipitated the sulphuric acid in lanthanum sulphate as barium sulphate. He found the atomic weight of lanthanum, from one determination, to be 133·4.

In the same year Choubine (*Journ. Prakt. Chem.*, 1842, xxvi., 443) published determinations of the atomic weight of lanthanum. He transformed the oxide into lanthanous chloride, and then precipitated the chlorine by means of silver nitrate. The two determinations gave values lower than that found by Rammelsberg, but Choubine's material was almost certainly contaminated with other substances.

The same criticism applies to the work of Hermann (*Journ. Prakt. Chem.*, 1843, xxx., 199), who, the following year, made a few determinations of the atomic weight of lanthanum.

The first determination of the atomic weight of lanthanum upon which much stress can be laid is that of Marignac (*Arch. Sci. Phys. et Nat.*, 1849, [1], xi., 29). He titrated solutions of lanthanum sulphate with a solution of barium chloride. As a mean of nine determinations he found the atomic weight of lanthanum to be 140·2.

Holzmann (*Journ. Prakt. Chem.*, 1858, lxxv., 343) attempted to determine the atomic weight of lanthanum by several methods. He analysed the sulphate by precipitating the lanthanum as oxalate, igniting the oxalate, and weighing the oxide. From three determinations he obtained for the atomic weight of lanthanum the value 138·8. He also analysed the iodate of lanthanum by precipitating the lanthanum as oxalate and determining the iodic acid volumetrically. The lower values found by this method cannot be regarded as important, since the method has been shown to be defective. Holzmann also determined the atomic weight of lanthanum by analysing the double nitrate of lanthanum and magnesium, $2La_2(NO_3)_3.3Mg(NO_3)_2.24H_2O$. This method, like that involving the use of the iodate, is open to serious objection.

In 1860 Czudnowicz (*Journ. Prakt. Chem.*, 1860, lxxx., 33) published one analysis of lanthanum sulphate, and a year later Hermann (*Journ. Prakt. Chem.*, 1861, lxxxii., 395) analysed both the sulphate and carbonate of lanthanum. Since the material was not purified with sufficient care, no stress can be laid upon the results obtained.

In 1868 Zschiesche (*Journ. Prakt. Chem.*, civ., 176) freed his lanthanum from didymium, and made six analyses of lanthanum sulphate. The values found for the atomic weight of lanthanum differ more than three units. The mean value is 135·9.

Erk (*Zeit. Chem.*, N.F., vii., 106; *Zeit. Anal. Chem.*, 1871, x., 509) analysed the sulphate of lanthanum by precipitating the lanthanum with ammonium oxalate, igniting the oxalate, and weighing the oxide. The mean of three determinations gave for the atomic weight of lanthanum the value 135·5.

Erk also determined the sulphuric acid in the filtrates, and from these results calculated the atomic weight of lanthanum to be 135·3.

Marignac (*Ann. Chim. Phys.*, 1873, [4], xxx., 68) redetermined the atomic weight of lanthanum by further purifying the sulphate by repeated crystallisation. In two determinations the sulphate was heated to dull redness, weighed, and then heated to a white heat to convert the sulphate into oxide. In two other determinations the dried sulphate was dissolved, and the solution treated with a solution of ammonium oxalate. The oxalate of lanthanum was strongly heated to convert it into the oxide, and the oxide weighed. By the first method Marignac obtained for the atomic weight of lanthanum the value 138·9; by the second method the value 138·7.

Clève (*K. Svensk. Akad. Handlingar*, 1874, ii., 7) made five determinations of the atomic weight of lanthanum in 1874. The oxide, analysed spectroscopically, was dissolved in nitric acid. The solution was treated with sulphuric acid, evaporated to dryness, and the residue heated to remove all excess of sulphuric acid. The amount of sulphate formed was then weighed. The mean of Clève's determinations gave, for the atomic weight of lanthanum, the value 139·3.

Brauner (*Monatsh. Chem.*, 1883, iii., 28) made his first determinations of the atomic weight of lanthanum in 1882. In two syntheses of the sulphate from the oxide he obtained for the atomic weight of lanthanum the values 138·94 and 138 83, the mean being 138·88.

In a second series of determinations published in the same year, Brauner (*Monatsh. Chem.*, iii., 493) obtained considerably lower values. With this material, which Brauner thinks was purer than that originally used, he obtained values for the atomic weight of lanthanum ranging from 138·06 to 138·45, with a mean of 138·28.

Clève (*Bull. Soc. Chim.*, 1883, xxxix., 151) published his second series of determinations of the atomic weight of lanthanum in 1883. The material which Clève used was unquestionably purer than any which had been employed up to that time. He made a series of twelve determinations by converting the oxide into the sulphate. The atomic weight of lanthanum calculated by Clève on the basis of $SO_3=80$ varied from 138·07 to 138·35, with a mean of 138·22. Calculated on the basis of the present values for oxygen and sulphur, this becomes 138·55. Of all the determinations of the atomic weight of lanthanum thus far made, this is apparently entitled to the greatest confidence.

Bauer (Dissertation, Freiburg, 1884), in 1890, made four determinations of the atomic weight of lanthanum by converting the oxide into the sulphate. The results calculated in terms of oxygen = 16 and sulphur = 32·06 range from 138·91 to 138·3.

Bettendorff (*Liebig's Ann. Chem.*, 1890, cclvi., 168) made four determinations of the atomic weight of lanthanum by the same method, *i.e.*, the synthesis of the sulphate from the oxide. He calculated the atomic weight of lanthanum on the basis of O = 15·96, S = 31·98, and obtained values ranging from 138 21 to 138·24. His results calculated on the present basis, of oxygen = 16 and sulphur = 32·06, give as the atomic weight of lanthanum the value 138 62.

Wolcott Gibbs (*Proc. Am. Acad.*, 1893, xxviii., 260) carried out, in 1893, an extensive investigation on the rare earths, with special reference to methods of separating and determining these substances. He analysed the colourless nitrate of ammonium and lanthanum furnished him by Dr. Shapleigh, by precipitating the lanthanum as oxalate and igniting the oxalate. He found for the atomic mass of lanthanum the value 139·7.

Gibbs does not seem to lay much stress upon this result as a determination of the atomic weight of lanthanum, since his work was carried out rather to test certain analytical methods than to purify the several elements and determine their atomic weights. Gibbs states (*Proc. Am. Acad.*, 1893, xxviii., 262) that Shapleigh found values of the same order of magnitude as his own by means of the sulphate method.

The most recent determinations of the atomic weight of lanthanum is that of Brauner and Pavlicek (*Proc. Chem. Soc.*, xvii., 63; also Chemical News, 1903, vol. lxxxvii.,

* From the *American Chemical Journal*, xxviii., No. 1.

p. 49, *et. seq.*). The material was purified by crystallising the double nitrate of ammonium and lanthanum. It was then fused with potassium sodium nitrate and fractionally precipitated with potassium hydroxide. Brauner determined the atomic weight of the lanthanum in the several fractions, and found it to vary from 138·78 in the most positive fraction to 139·1 in the most negative. They regard the most positive fraction as representing the purest lanthanum. They, however, think that since the sulphate is hygroscopic, from 0·2 to 0·3 should be added to the value found by experiment. When this is added to 138·78 they obtained 139·0, which they regard as the true atomic weight of lanthanum.

Brauner and Pavlicek conclude that the sulphate method of determining atomic weights, as ordinarily applied, is unreliable, since the sulphate always contains acid sulphate. They used the sulphate method, but determined the amount of acid sulphate present by titrating with sodium hydroxide, and introducing the corresponding correction.

This conclusion, we shall show, is not based upon a sufficient study of the facts. The presence or absence of acid sulphate depends upon the temperature to which the sulphate has been heated.

It is obvious, from the above sketch of what has been done, that the question of the atomic weight of lanthanum is far from settled. Take even the more recent and trustworthy determinations, and we find a lack of concordance amounting to several units. A careful study of these investigations will show that this is probably due to the different degrees of purity of the materials employed.

Material Used.

The present investigation would not have been undertaken but for the fact that an unusually pure specimen of lanthanum was placed at the writer's disposal by Dr. Waldron Shapleigh, just before his death.

I should like to take this opportunity to express my many obligations to Dr. Shapleigh, in connection with the work already done on the atomic weights of the so-called "rare earths." He isolated lanthanum, praseodymium, neodymium, thorium, and cerium on a scale never dreamed of before his time, and placed the fruit of a score of years at the disposal of those who desired to carry out purely scientific investigations, with a liberality which is rare. Scientific, as well as technical, chemistry, has suffered an irreparable loss by the death of this most genial man.

In addition to having at my disposal remarkably pure ammonium lanthanum nitrate by the kilogramme, the unusual spectroscopic facilities offered by the physical department of this University, in the Rowland spectroscope, made it highly desirable that the atomic weight of lanthanum should be carefully studied.

The double nitrate of ammonium and lanthanum was subjected to fractional crystallisation until spectrum analysis showed that it was homogeneous, and contained as impurity only a trace of cerium. The double nitrate was heated in small quantities over the blast-lamp until only the oxide of lanthanum remained.

To remove any trace of the nitrate which might not have been decomposed, the resulting oxide was boiled for a considerable time with water which had been purified by the method described by Jones and Mackay (*Am. Chem Journ.*, 1897, xix., 91) for preparing water for conductivity measurements. Indeed, all the water used in this work was purified by this method.

The oxide was filtered off and thoroughly washed with hot water. It was then treated with hot, dilute nitric acid, and dissolved, leaving, however, a slight cloudiness, which was basic cerium nitrate. The solution was then filtered repeatedly through the same filter until it was perfectly clear.

The solution of the nitrate was then treated with a dilute solution of oxalic acid, which had been purified as follows:—Commercial oxalic acid was dissolved in redistilled, cold water. The solution was concentrated by evaporation, and crystals of the acid obtained. The crystals were then dissolved in a mixture of equal parts of pure anhydrous ethyl alcohol and pure anhydrous ether. In this way the oxalic acid was freed from every trace of metallic salts.

To the solution of the oxalic acid in alcohol and ether 3 to 4 volumes of water were added, and the mixture boiled for some time, until the ethyl oxalate formed had been decomposed. The solution was then evaporated, and the oxalic acid allowed to crystallise.

The oxalate of lanthanum was precipitated from the nitrate in the presence of nitric acid. In this way it was separated from all of the more common impurities, such as calcium, iron, &c.

The oxalate was then decomposed to the oxide and analysed spectroscopically by Mr. L. E. Jewell, whose work in this field is so well known. The only impurity which could be detected was a trace of cerium, and this was not more, and probably much less, than 0·01 per cent.

The oxalate was again decomposed to the oxide, the oxide dissolved in hot dilute nitric acid, and the lanthanum precipitated again as the oxalate. The oxalate was decomposed over the blast-lamp, and the resulting oxide used for the following determination :—

To determine whether the oxide prepared in this way contained any oxide richer in oxygen than the sesquioxide, a specimen was heated in an atmosphere of hydrogen. The oxide was placed in a porcelain boat, and the whole weighed. The boat was shoved into a hard-glass tube, and the tube heated in a combustion-furnace until the glass began to soften; a stream of hydrogen, purified by passing through solutions of sodium plumbate and silver nitrate, and dried, being led through the tube. After the oxide had been heated to redness for about an hour it was allowed to cool in an atmosphere of hydrogen, and then placed in a desiccator over phosphorus pentoxide until weighed. No loss in weight could be detected. The oxide was then returned to the glass tube and re-heated for a second hour in an atmosphere of hydrogen. It maintained perfectly constant weight. From these experiments the conclusion was drawn that the oxide of lanthanum prepared by decomposing the oxalate is the pure sesquioxide, free from any higher oxide.

Carrying out a Determination.

The glaze was removed from the inside of a porcelain crucible by treating it with hydrofluoric acid, and the resulting dust brushed out with the greatest care. Indeed, the crucible was scoured with a button-brush turned in a lathe, until every particle of loose material had been removed. This was done to prevent the oxide of lanthanum from coming in contact, while hot, with the glaze on the crucible and the possible formation of a silicate of lanthanum. The glaze was not removed from the exterior of the crucible, since its presence prevented any reducing gases from the flame from passing through the porcelain and coming in contact with the oxide.

The desired amount of lanthanum oxide was placed in the porcelain crucible, and heated over the blast-lamp to constant weight.

A platinum crucible was placed in a weighing tube with a ground-glass stopper, and weighed. The oxide of lanthanum was quickly transferred from the porcelain crucible, in a desiccator containing phosphorus pentoxide, to the plantinum crucible. The latter was quickly introduced into the weighing tube, and the whole re weighed. In this way the weight of the oxide used in an experiment was determined.

The weighings were made to 0·00005 grm. The writer is of the opinion that this is sufficiently accurate for refined atomic weight determinations, since every chemist

s fully aware that the most accurate operation carried out in a chemical laboratory is the weighing with a satisfactory balance. The weighings were made to 0·05 m.grm., and the 0·1 m.grm. nearest to the value found was taken as the true weight. The error in weighing was thus quite as small as in the remaining operations connected with the carrying out of the method.

The oxide was then treated with a measured volume of fairly concentrated sulphuric acid, and warmed very gently until it had been transformed into the sulphate. Unless this precaution is taken the reaction is liable to take place with some violence and cause the substance to spatter upon the sides and top of the crucible. The sulphate was then evaporated slowly to dryness in an upright air-bath, the crucible resting upon a porcelain triangle about 2 c.m. from the bottom of the bath. The sulphate was then heated sufficiently high to decompose all acid sulphates which might have been formed. It was then re-heated until constant weight was established.

Proof of the Absence of Acid Sulphates.

The question of the presence of acid sulphates of lanthanum was studied with care, especially since Brauner (*Proc. Chem. Soc.*, xvii., 63; *Centrbl.*, 1901, 1035) had stated that under these conditions Wyrouboff's acid sulphate was always present. Indeed, Brauner and Pavlicek determined the amount of the acid sulphate present under the conditions with which they worked by titration with sodium hydroxide.

The sulphate of lanthanum which had been heated to constant weight was at first treated with a few drops of a solution of ammonium carbonate, and re-heated. It lost in weight very considerably, and continued to do so as more and more ammonium carbonate was added. This led to the conclusion that the lanthanum sulphate was undergoing decomposition in the presence of ammonium carbonate, giving rise to lanthanum carbonate and ammonium sulphate which was volatilised at the temperature employed. This was proved by the fact that when the lanthanum sulphate was dissolved in water a very considerable insoluble residue remained behind. Indeed, this is just what we would expect when we consider that lanthanum is such a weak base. This is the probable explanation of the fact pointed out by Brauner and Pavlicek that when ammonium carbonate was added to lanthanum sulphate, which had been heated to 450°, a further loss in sulphuric acid took place.

The method of testing for the presence of acid sulphate was the following:—The sulphate was heated to constant weight, and dissolved in water. The solution was perfectly clear, showing that none of the sulphate had been decomposed. The solution was then tested to see whether it would show an acid or basic reaction. In every determination the solution of the sulphate was found to be perfectly neutral, showing not the slightest trace of acid or basic properties.

These facts, together with the complete solubility of the sulphate, show that we had to deal with the normal sulphate, free from both acid and basic salt.

A volume of the sulphuric acid just equal to that used in each determination was evaporated to dryness, and the residue weighed. The residue was found to weigh 0·00002 grm.

(To be continued).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., His Grace the Duke of Northumberland, President, in the Chair. The following were elected members:—Miss M. G. Anderson, Mr. Harold Brown, Mr. T. W. Chitty, Mr. H. T. Crosby, Mr. R A. Hatfield, Mr. W. W. Pope, Miss S. F. de Rodes, and Mrs. G. Orr Wilson.

VOLUMETRIC ESTIMATION OF "TRUE" CASEIN AND OF OTHER ALBUMENOIDS IN MILK.

By M. DENIGÈS.

The method which consists of estimating the total nitrogen in a milk to arrive at its nutritive value, is not founded on a sound principle. In fact, we may agree with Danilewski that only the albumenoid substances, properly so-called, have any nutritive value, while certain peptonic substances, still retaining the property possessed by albumenoids of precipitating Tanret's reagent, have no alimentary value at all. Now, in milk we meet with proteïc matters, much more degraded than the peptones, of which the molecule is sufficiently different from the true albumenoids as not to precipitate the above-mentioned reagent. These substances cannot be regarded as improving the alimentary value, still they are included in the total nitrogen. Thus, it is much more rational to effect the estimation of the nitrogenous principles precipitable by Tanret's reagent or an iodo-mercuric solution in acetic acid.

To effect this estimation of the true casein, the author recommends the method he described in 1896, but modified into two operations, to estimate and separate the true casein and the non-precipitable albumenoids in the cold with acetic acid. These two operations are as follows:—

First Operation.—Twenty-five c.c. of milk and 1 c.c. of a 30 per cent solution of neutral oxalate of potassium are put into a graduated matrass of 200 c.c. capacity; 20 c.c. of solution are added, prepared from 13·55 grms. of bichloride of mercury, 36 grms. of iodide of potassium, and water to make 1 litre; 2 c.c. of glacial acetic acid are added to the matrass, and water is added to 200 c.c.; shake well and filter. One hundred c.c. of the filtrate are then placed in a conical flask of 250 or 300 c.c. capacity, containing 10 c.c. of a solution of cyanide of potassium equivalent to a decinormal solution of nitrate of silver, and 15 c.c. of ammonia. By means of a burette, $\frac{1}{10}$th N solution of nitrate of silver is run in until the faint cloudiness is persistent. Let *a* be the number of tenths of a c.c. of this solution used, a number always greater than 48; from *a* subtract 48, and compare the figure thus obtained with the following table, which gives immediately in grms. per litre the total albumenoids contained in the milk:—

Values of *a*−48.	Albumenoids per litre.	Values of *a*−48.	Albumenoids per litre
0	0	24	22·25
1	1	25	23·50
2	1·75	26	24·75
3	2·50	27	26
4	3·	28	27
5	3·75	29	28
6	4·50	30	29·25
7	5·50	31	30·75
8	6·50	32	32
9	7·15	33	33·50
10	8	34	35
11	9	35	37
12	10	36	39
13	11	37	40·50
14	12	38	42·75
15	13	39	45
16	14	40	47
17	15	41	49
18	16	42	51·50
19	17	43	54
20	18	44	57·20
21	19	45	60
22	20	46	62·50
23	21		

Second Operation.— To obtain the albumenoids not precipitable by acetic acid, we put into a 250 c.c. matrass 50 c.c. of milk, about 180 c.c. of water, and shake well; add 0·2 c.c. of glacial acetic acid, and water up to the 250 c.c. mark; shake well a second time and filter. We take 125 c.c. of this filtrate, which represents 25 c.c. of milk, put it in a 200 c.c. matrass, add 1 c.c. of a 30 per cent solution of oxalate of potassium, 20 c.c. of mercuro-potassic iodide, and 2 c.c. of glacial acetic acid; make up to 200 c.c. with water, shake well, filter, and finish the operation as above.

The new value, *b*, of the nitrate of silver used, still diminished by subtracting the constant 48, gives, by the aid of the table, the amount of albumenoids per litre of milk not precipitable by acetic acid.

Let A be the figure representing the total albumenoids in the milk under examination, and B the figure representing the albumenoids not precipitable by acetic acid; then A—B will give the proportion of "true" casein contained in 1 litre of milk. In the same way we might determine, after filtration, the albumenoids in the milk not coagulated by pressure, from which we could deduce the amount of proteic coagulate, which is of great importance in the manufacture of cheese.—*Revue Internationale des Falsifications*, 16th Year, Jan.-Feb., 1903, p. 18.

COMBUSTION IN GASEOUS MIXTURES OTHER THAN AIR.

By L. PELET and P. JOMINI.

In a previous paper (*Bull. Soc. Chim.*, 1902, p. 1207) we considered the causes of the extinction of flames in the air. In the present research we have endeavoured to find at what point the extinction of a flame takes place when a combustible material burns in a mixture of oxygen, nitrogen, and carbonic anhydride in variable proportions.

We have proceeded in these experiments as in the former ones, but we give the results of our analyses just as we obtained them, without reduction.

First Series.—In a bell-jar of 12 litres capacity, containing air previously charged with CO_2, we burnt a candle until it became extinguished. The analysis of the gas was made before and after combustion took place.

Air charged with— CO_2, per cent.	The combustion lasted— Seconds.	Gases estimated after combustion. CO_2, per cent.	O, per cent.	N, per cent.
2·5	90	4·3	16·5	79·2
3·5	60	5·4	16 2	78·4
6·2	12	6·9	17·0	76·1
8·0	8	8·3	17·3	74·4
10·8	1	10·8	17·0	72 2
11·8	0	11·8	17·0	71·2

Second Series.—Replacing the air charged with CO_2 by a mixture of oxygen and nitrogen.

Gases estimated before combustion. O.	N.	Combustion lasted—	Gases estimated after extinction. CO_2.	O.	N.
Per cent.	Per cent.	Seconds.	Per cent.	Per cent.	Per cent.
20·8	79·2	120	3·6	16 0	80·2
25	75	150	6·0	17·0	77 0
30	70	225	8·4	17 6	74·0
40	60	300	27 8	19·5	52 7
50	50	360	32 0	20·7	47·3
60	40	370	33·0	20·7	46·1
65	35	370	34·1	20·7	45·3
70	30	380	34·9	20 6	44·5
80	20	380	50·0	21·2	27·9
90	10	380	52 0	21·1	26·0

Third Series.—We checked these results by burning a candle in mixtures of oxygen and carbonic anhydride.

Gases estimated before combustion. CO_2.	O.	N.	Combustion lasted—	Gases estimated after extinction. CO_2.	O.	N.
Per cent.	Per cent.	Per cent.	Seconds.	Per cent.	Per cent.	Per cent.
40	21	39	0	40	21	39
65	22	13	1	65	21	14
50	36	14	100	60·2	20·8	19
25	75	0	300	78	22	—
50	50	0	120	78	22	—
65	35	0	90	78	22	—
70	30	0	60	78	22	—
75	25	0	0	75	25	—

From these figures it appears that a candle is able to burn in the presence of quantities of carbonic anhydride (less than 75 per cent) so long as 16 to 22 per cent of unburned oxygen remains in the gaseous mixture. We see that the different authors, who have stated that the extinction of the flame of a candle or petroleum lamp occurs at fixed proportions of carbonic anhydride, have only considered one aspect of the problem. On this subject we have found the following statements:—Eulenberg asserts that extinction occurs at 3 per cent of CO_2; Gaertner, at 2·2 to 7 per cent; Emmerich, at 8 per cent; Taylor, at 10 per cent; Graham-Otto, at 20 per cent; and Arnould, at 25 per cent. (*Journal für Gasbeleuchtung*, 1900, p. 335; 1901, p. 332; Graham-Otto, "Lehrbuch der Chemie," vol. ii., p. 719; Arnould, "Elements d'Hygiene," p. 179).

In his examination of the air of mines (*Ann. Chim. Phys.*, [3], 1845, xv., p. 488), Felix Leblanc was the only one, so far as we know, who has interpreted the facts in a correct manner. He says:—"It is the amount of oxygen that has disappeared that determines the resistance to combustion. At 17 per cent of oxygen (remaining) the combustion of lamps (of miners) is no longer sustained if the oxygen used has been replaced by its own volume of carbonic acid or by nitrogen."

We have completed the examination of this subject by using other combustible materials besides candles.

Fourth Series.—Combustion of an alcohol flame in air charged with carbonic anhydride in an enclosed space of 12 litres.

Air charged with— CO_2, per cent.	Combustion lasted— Seconds.	Gases estimated after extinction. CO_2, per cent.	O, per cent.	N, per cent.
4 0	8	6·7	14·3	79·0
6·5	4	6 8	14·4	78·8
7 0	6	7·2	15·3	77·5
11·4	1	11·4	15·4	74·0
13·3	0	13·3	15·3	71·4

Fifth Series.—Combustion of an alcohol flame in a mixture of oxygen and nitrogen in an enclosed space of 12 litres.

Gases estimated before combustion. O.	N.	Combustion lasted—	Gases estimated after extinction. CO_2.	O.	N.
Per cent.	Per cent.	Seconds.	Per cent.	Per cent.	Per cent.
30	70	60	12·0	12·3	75·7
40	60	75	14·3	12 3	72·4
45	55	80	14·8	13·8	71·4
50	50	90	20·3	13·0	66 7

Sixth Series.—Combustion of lighting gas (butterfly flame) in air charged with carbonic anhydride.

Air charged with— CO_2, per cent.	Combustion lasted— Seconds.	Gases estimated after extinction. CO_2, per cent.	O, per cent.	N, per cent.
8·0	40	10·4	11·0	78·6
10 0	20	12·0	11·0	77 0
13·0	10	13 0	11·3	75·7
25·0	0	25·0	12·5	61·5

Seventh Series.—Combustion of lighting gas (butterfly flame) in a mixture of oxygen, nitrogen, and carbonic anhydride.

Gases estimated before combustion.			Combustion lasted—	Gases estimated after extinction.		
CO_2.	O.	N.		CO_2.	O.	N.
Per cent.	Per cent	Per cent.	Seconds.	Per cent.	Per cent.	Per cent.
0	40	60	40	13·0	10·9	75·2
0	50	50	42	12·5	11·2	75·5
0	55	45	50	14 8	10·7	74·5
0	60	45	50	14·8	11·2	74·5
24	40	36	50	34·4	11·2	54·4

We observe again that, whether in the combustion of alcohol or in that of gas, the flame is able to maintain itself in the presence of very variable quantities of carbonic anhydride, so long as there remains a certain proportion of unconsumed oxygen in the gaseous mixture.

In the case of alcohol, the minimal proportion of oxygen remaining was from 12 to 15·3 per cent; and in the case of lighting gas, from 10·7 to 12·5 per cent. For the present, we are not aware of the causes of the variations of the proportion of residual oxygen; the experimental material is, in fact, too much combined, and the different factors which determine the extinction of the flame too multiplex for us to attempt to apply the laws of chemical equilibrium in these preliminary researches.

In a general way, we may attribute the variations of the minimal proportion of remaining oxygen to the temperature of the flame, to the temperature of the air or gaseous mixture, and to the paralysing action of the carbonic anhydride formed in the reaction $C+O_2=CO_2$.

The changes of the flame before extinction give interesting data on the modifications of the combustion. As a general rule, the flames die out while becoming longer, smoking, and, what is very curious, when the combustion is taking place in the presence of a certain proportion of carbonic anhydride, the hydrogen of the hydrocarbonised products burns alone, forming water, and the proportion of carbonic anhydride formed increases very little or not at all. This fact is especially characteristic of the last experiment but one in the sixth series, where we see that the proportion of CO_2 is the same both before and after the combustion.

In the last experiment of the seventh series, the increase of carbonic anhydride is only apparent; it is caused exclusively by the disappearance of 30 per cent of oxygen converted into water vapour which was not estimated. Thus the combustion took place entirely at the expense of the hydrogen. We intend examining these various points more completely.

To sum up, we may state that:—

1. The combustion of a flame can be maintained in the presence of varying quantities of carbonic anhydride (from 0 to 75 per cent) so long as there remains a definite proportion of unburned oxygen in the gaseous mixture.

2. For the same combustion, the minimum proportion of unburned oxygen at which extinction occurs varies within small limits.

3. For different combustions, the proportion of residual oxygen corresponding to the extinction will be inversely proportional to the limit of combustibility (temperature of the flame, &c.).—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 5.

IMPROVEMENT IN THE USE OF SCHÖNBEIN PAGENSTECHER'S TEST-PAPER TO DETECT TRACES OF HYDROCYANIC ACID GAS.

By J. C. BRÜNNICH, F.C.S.,
Department of Agriculture, Brisbane, Queensland.

Schönbein Pagenstecher's test-paper was found very useful to prove the presence of hydrocyanic acid in some of our fodder plants—sorghum, maize, &c.—as a prelinary qualitative test in connection with the quantitative determination. An exhaustive investigation with fodder plants at various stages of growth is being carried out in the Departmental Laboratory by the author, in connection with the Director, Dr. W. Maxwell.

For the determination of the hydrocyanic acid the plants are quickly cut into slices, minced pretty fine, and mixed with weighed quantities of water in a well-stoppered bottle. After a very short time, under fermentative action, hydrocyanic acid is liberated, which is at once detected by the faint blue colouration on strips of the test-paper suspended from the stopper. The quickness and intensity of the colouration gives a fair guide to the quantity of the poison present in the plants. No hydrocyanic acid is liberated from the mixture if a small amount of formalin is added to the water, and the suspended test-paper remains perfectly white even after two or three days' standing. Thinking that perhaps formaldehyde vapours might interfere with the efficacy of the test-papers, I made a blank experiment to test the effect of formalin on the test-paper, and I found that it increases the sensitiveness of the paper enormously, and that if the Schonbein Pagenstecher's test-papers are moistened with formalin, instead of using water, the presence of the faintest traces of HCN produces instantly a deep blue colour on the papers; this colour differing from the light blue produced if the papers are moistened with water. The blue colour fades slowly, disappearing finally, if the paper is exposed to the air, but is again reproduced by the presence of HCN.

Fumes of concentrated nitric acid and of bromine produce a similar colour, the blue changing into a yellowish and greenish tint after longer exposure.

Other liquids were used to moisten the test-papers, and I found that alcohol and ether act similarly to formalin, although not so intensely, whereas chloroform and turpentine have the same effect as water in producing the faint blue only in the presence of hydrocyanic acid gas.

ON CERIC CHROMATE.*

By PHILIP E. BROWNING and CHARLES P. FLORA.

Böhm (*Zeit. Angew. Chem.*, xv., 1282) in a recent paper descriptive of his thorough investigations of the application of chromic acid to the separation of the cerium earths, states that when the mixed oxides of cerium, lanthanum, and didymium are brought in contact with a calculated amount of chromic acid, a little water added, and heat applied for a time, an orange-red amorphous powder remains which proves to be a basic ceric chromate. In connection with a study of the methods of separating the cerium earths, begun last summer, we had occasion to make an experiment similar to that described by Böhm, differing possibly in this respect—that we used a decided excess of the chromic acid (100 grms. of the oxides with 150 grms. of chromic acid and 200 c.m.³ of water).

The product which we obtained was a bright scarlet crystalline salt, which, when washed sparingly with water and dried over sulphuric acid, became a little darker in colour, but retained its crystalline condition. Examined under the microscope, the salt appeared homogeneous, and the crystalline form orthorhombic, the prevailing habit being prismatic, $m \wedge m'''$, $110 \wedge \bar{1}10$, being approximately 58° C. The macropinacoid, *a* (100), is generally present; the brachypinacoid, *b* (010), is well developed; and a flat brachydome and the basal plane, *c* (001), are the terminating forms. The crystals are etched or pitted, are slightly pleochroic, and exhibit parallel extinction and low birefringence. When treated with water, the salt loses chromic acid and becomes an orange-yellow. It may be heated to about 150° C. without loss of weight. Between 150° and 180° C. it loses water and becomes

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, [4], vol. xv., No. 87.

brownish red, still retaining much the same original exterior form. Above 180° C. it decomposes. It is quite readily soluble in dilute acids, especially sulphuric acid, and is easily decomposed by potassium or sodium hydroxide into the alkali chromate and ceric hydroxide. The ceric hydroxide thus formed is quite readily soluble in acids, and promises to be a convenient starting point for the preparation of ceric salts. Qualitative tests proved the absence of both yttrium and didymium.

Analysis of the salt gave the following results :—Five closely agreeing determinations of water, six determinations of ceric oxide, among which the greatest variation was about 1 per cent, and sixteen determinations of chromic acid showing as the greatest variation about 2 per cent, gave the averages tabulated below :—

	Salt examined.	$Ce(CrO_4)_2 2H_2O$ calculated.
CeO_2	41·94	42·14
CrO_3	49·61	49·04
H_2O	8·82	8·82
	100·37	100 00

From these analyses we feel justified in assuming the crystalline salt to be a close approximation to a compound whose constitution would be expressed by the symbol $Ce(CrO_4)_2 2H_2O$.

The material from which the mixed oxides used in this work were obtained was a mixture of sulphates of cerium, lanthanum, and didymium, carrying a trace of yttrium.

The authors are indebted to Mr. J. C. Blake for the crystallographic examination.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, March 18th, 1903.

Prof. J. EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

MESSRS. J. M. Wadmore, J. Phelps, and F. Soddy were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Wm. Lester St. John Alton, Dungarvan, Putney Heath, S.W.; Henry Gough, c/o Messrs. J. Lovibond and Sons, Ltd., Greenwich, S.E.; William Kirkby, Winster House, Thornfield Road, Heaton Moor; John George Collcutt Lock, 17, Berners Street, W.; George G. Pond, M.A., Ph.D., State College, Pennsylvania, U.S.A.; Robert James Porter, 11, Arlington Street, Hull; Ernest William Sawdon, B.Sc., 2, Esk Terrace, Whitby; Giles Hadden Welsford, 6, The Orchard, Blackheath, S.E.

The PRESIDENT stated, in reference to a petition which had been recently presented to the Council, that he had the authority of the Council to communicate to the Society the terms of the petition and of the resolution of the Council with regard to it. The terms of the petition were :—

"We, the undersigned Fellows of the Chemical Society, being of opinion that the interests of the general body will be promoted by limiting the period of service of the Honorary Secretaries and Foreign Secretary, do hereby request the Council to earnestly consider the desirability of so limiting the tenure of office."

The resolution passed by the Council *nem. con.*, which was duly communicated to Mr. C. E. Groves, who represented the petitioners, was "That this Council is of opinion that the tenure of office of the Officers of the Society should not be indefinitely extended, but that it is not desirable to limit the period by assigning a definite term of years to the tenure of each office."

Of the following papers, those marked * were read:—

*45. "*Essential Oil of Hops.*" By A. C. CHAPMAN.

Since the publication of the earlier results of the study of oil of hops (*Proc.*, 1893, 177; *Trans.*, 1895, lxvii., 54 and 780), three more samples of oil of undoubted genuineness have been examined. These had the following specific gravities and specific rotations :—

	Sp. gr. 15°/15°.	Sp. gr. 20°/20°.	$[\alpha]_D$ 20°.
No. 5	0·8676	0 8645	+0·30°
No. 6	0·8639	0·8610	−0·20°
No. 7	0·8403	0·8357	−0·08°

The fraction of lowest boiling-point, obtained after prolonged fractional distillation under reduced pressure, consisted of a hydrocarbon $C_{10}H_{16}$, which had the following properties :—Sp. gr. 0·8046 at 15°/15° and 0·8020 at 20°/20°; b. p. 74—75° (33 m.m.) and 166—168° (774 m.m.), undergoing at the same time slight polymerisation. It was optically inactive, and had a refractive index 1·4645 at 20°, and a molecular refraction 46·8, the calculated number for $C_{10}H_{16}$ (with 3 double linkings) being 46·78. This compound is therefore an aliphatic hydrocarbon, and its properties are almost identical with those of myrcene; it absorbs oxygen from the atmosphere, and readily undergoes polymeric change, becoming converted into a colourless resin.

The next fraction (b. p. 120—130°, 46 m.m.) was a very small one, and gave on analysis numbers agreeing with the formula $C_{10}H_{18}O$. It had a sp. gr. 0·8571 at 20°/20°, produced a rotation of −0° 40′ in a 100 m.m. tube, and evidently consisted of inactive linalool mixed with a small quantity of some active substance.

The third small fraction (b. p. 135—150°, 46 m.m.) consisted of an ester, and yielded on saponification *iso*nononoic acid, $C_9H_{18}O_2$, and linalool, together with a small quantity of geraniol.

The highest and largest fractions in all three samples of oil consisted of nearly pure humulene. On submitting the oil to the action of boiling chromic acid mixture, it yielded acetic, valeric, succinic, unsymmetrical dimethylsuccinic (m. p. 140°), and *iso*nononoic acids, the last of these having been probably derived from the linalyl ester. When dilute nitric acid was employed in the oxidation, oxalic and acetic acids were the chief soluble products of acidic character.

Oxidation experiments made with the fractionated constituents of the oil showed that the dimethylsuccinic acid is derived from the humulene, and succinic acid from the myrcene.

The essential oil of hops therefore contains the following compounds :—Myrcene, humulene, linalool, linalyl *iso*nonoate, with small quantities of a diterpene, and probable traces of some ester of geraniol.

In all the freshly distilled samples of oil examined, the hydrocarbons myrcene and humulene were present to the extent of from 80 to 90 per cent.

DISCUSSION.

Dr. POWER remarked that the results obtained by Mr. Chapman seemed to leave no doubt respecting the identity of the hydrocarbon of low boiling-point contained in hop oil with the myrcene of oil of bay. Attention was also called to the fact that, apart from the interest connected with the general properties of myrcene and the occurrence of such an olefinic terpene in nature, it has recently been utilised in a study of the chemical composition of Para rubber. Harries (*Ber.*, 1902, xxxv., 3259) has shown that when rubber is treated with nitrous acid it yields a series of nitrosites, one of which has the molecular composition $(C_{10}H_{15}O_7N_3)_2$, and appears to be identical in every respect with a nitrosite obtained from a product of the polymerisation of myrcene termed dimyrcene, $C_{20}H_{32}$. It is thus rendered probable that myrcene stands in very close relationship to isoprene and caoutchouc.

In reply to Professor Tilden, Mr. CHAPMAN said that he

had not obtained any evidence of the existence of pinene in the oil. The slight optical activity was, in all probability, due to the presence of a small quantity of active linalool, but the intermediate fractions were so small, even when working with considerable quantities of the oil, that it was impossible to arrive at a definite conclusion in regard to this point.

*46. "*A Compound of Dextrose with Aluminium Hydroxide.*" By A. C. Chapman.

The author has obtained a compound of dextrose with aluminium hydroxide by the following process:—

To a solution of 8 grms. of pure anhydrous aluminium chloride in about 1500 c.c. of 90 per cent alcohol, powdered dextrose was added until it no longer dissolved after allowing the mixture to remain some time in a warm place. The white, gelatinous precipitate immediately produced by adding aqueous ammonia in slight excess to the filtered solution was collected, washed with 90 per cent alcohol, and dried until of constant weight in an exhausted desiccator over sulphuric acid. It was not found possible by repeated washing to remove the last trace of chlorine, a small quantity invariably remaining, apparently in the form of a basic chloride. By careful treatment it is, however, possible to obtain a preparation which, after drying, will not contain more than 0·2 to 0·5 per cent of chlorine.

Many different preparations of this compound were made with slightly varying proportions of dextrose and aluminium chloride. The analytical results, although fairly concordant, do not correspond with any simple formula:—

	C=	H=
1. 0·6010 gave 0·376 CO_2 and 0·276 H_2O.	17·06;	5·10.
2. 0·4270 ,, 0·275 CO_2 ,, 0·196 H_2O.	17·56;	5·08.
3. 0·4135 ,, 0·264 CO_2 ,, 0·185 H_2O.	17·41;	4·96.
4. 0·6010 ,, 0·250 Al_2O_3; Al=22·01.		

Three other estimations gave Al=22·12, 22·18, and 22·34. $[3C_6H_{12}O_6,5Al_2O_3,11H_2O]$ requires C=17·39; H=4·67; Al=21·80 per cent.

From these results, it appears probable that the white, flocculent precipitate is a compound of 3 mols. of dextrose with 5 mols. of aluminium hydroxide $[3C_6H_{12}O_6,5Al_2(OH)_6]$, and that this compound, when dried, in an exhausted desiccator over sulphuric acid, loses approximately 4 mols. of water (compare *Trans.*, 1889, lv., 576; 1891, lix., 224).

This aluminium compound is a white, amorphous substance, insoluble in water and alcohol, but dissolving in dilute acids. It differs from the similar compounds of dextrose with the oxides of iron and chromium in being insoluble in water when freshly precipitated; with boiling water it undergoes partial decomposition into aluminium oxide and dextrose. On drying for some hours at 100°, the substance lost 12 per cent of its weight, and acquired a pale yellow colour, but did not char appreciably at this temperature; it burned with extreme readiness when heated more strongly, yielding a mixture of the metallic oxide mixed with carbon, the final residue after prolonged ignition consisting of aluminium oxide.

*47. "*Action of Phosphorus Haloids on Dihydroresorcin.* Part II. *Dihydroresorcin.*" By A. W. Crossley and P. Haas.

Dihydroresorcin behaves towards phosphorus haloids in a similar way to its dimethyl derivative (*Trans.*, 1903, lxxxiii., 110), in fact, as if it possessed the following formula:—$CH_2<\begin{matrix}CH_2\text{—}CO\\CH_2\cdot C(OH)\end{matrix}>CH$.

5-Chloro-3-keto-Δ^4*-tetrahydrobenzene*,—

$$CH_2<\begin{matrix}CH_2\text{—}CO\\CH_2\cdot CCl\end{matrix}>CH,$$

obtained by the action of phosphorus trichloride on dihydroresorcin, is a colourless, highly refractive liquid boiling at 104° (24 m.m.); it gives a *semicarbazide* melting at 190°, and on oxidation is converted into glutaric acid.

The corresponding *bromo*-derivative boils at 132·5—133° (52 m.m.).

Phosphorus pentachloride gave rise to 3:5-*dichloro-*Δ^2:4-*dihydrobenzene*, $CH_2<\begin{matrix}CH=CCl\\CH_2\cdot CCl\end{matrix}>CH$, a colourless refractive liquid boiling at 88—90° (29 m.m.). On treatment with excess of phosphorus pentachloride or with bromine, it was converted into *m*-dichlorobenzene, and on reduction with sodium in moist ethereal solution, yielded a mixture of di- and tetra-hydrobenzenes. This mixture of hydrocarbons readily absorbed two atoms of bromine, and the resulting liquid deposited crystals of *dibromodihydrobenzene*, $C_6H_8Br_2$, which separated from light petroleum in transparent, hexagonal prisms melting at 104·5°, and decomposing at 170° with evolution of hydrogen bromide.

*48. "*The Constitution of Cotarnine.*" By J. J. Dobbie, A. Lauder, and C. K. Tinkler.

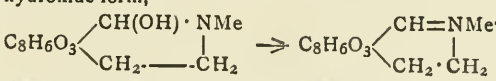
Although previous investigators are in agreement as to the possible existence of the carbinol form of cotarnine, the question as to whether this constitution or one expressed by an open change formula should be assigned to solid cotarnine has hitherto remained unsettled. A satisfactory answer has now been furnished by the study of the absorption spectra of this substance and its derivatives. Solid cotarnine begins to undergo a constitutional change as soon as it comes into contact with water or alcohol, but is not altered either by ether or chloroform, and the spectra of the ethereal and chloroform solutions, which may therefore be regarded as the true spectra of cotarnine, agree perfectly with one another, and also with those of hydrocotarnine and its salts; moreover, they are identical with those of the cyanide and ethoxyhydrocotarnine, these substances having been regarded as derivatives of the carbinol form.

The spectra of dilute aqueous or alcoholic solutions of cotarnine and those given by a solution of cotarnine hydrochloride from which the chlorine has been removed by means of silver oxide, are almost identical with the spectra of cotarnine hydrochloride, which, on the other hand, differ widely from the spectra of cotarnine in ether.

Cotarnine and all its derivatives hitherto examined spectroscopically conform to one or other of these two forms of spectra. (i.). The spectra of cotarnine in aqueous or alcoholic solution and of cotarnine salts show a large amount of general absorption with two well-marked absorption bands, one of which is close to the visible region. (ii.). The spectra of cotarnine in ether or chloroform, hydrocotarnine, ethoxycotarnine, and cotarnine cyanide show less general absorption than the former, and have a band much further removed from the visible region.

The substances in the first class are yellow, those in the second are colourless; the latter can all be represented as having a carbinol constitution.

When cotarnine is dissolved in anhydrous alcohol, it changes from the carbinol to the quaternary ammonium hydroxide form,—



the re-arrangement being promoted either by increasing the mass of the alcohol present or by heating. The transformation is effected much more rapidly by methyl than by ethyl alcohol.

A colourless solution of cotarnine in alcohol cannot be obtained, but since this isomeric change proceeds slowly, it is possible in ethyl alcohol, by photographing the freshly prepared solution immediately, and again after successive intervals of time, to trace the transformation through all its phases. The rate of progress of the change may even be determined by comparing photographs of the alcoholic solution with those of the spectra of mixtures of the solutions of the hydrochloride (ammonium form) and the cyanide (carbinol form) in known proportions. Potassium, sodium, and barium hydroxides, and even ammonia,

promote the reverse change to that effected by alcohol. When cotarnine hydrochloride in solution is decomposed by sodium hydroxide, the cotarnine changes at once to the carbinol form, but if an aqueous solution of cotarnine is treated with successively larger quantities of this alkali, the reverse change is gradual, and, as in the case of the opposite change induced by alcohol, can be distinctly traced through its various phases. These results explain several of the peculiarities observed by Hantzsch and Kalb (*Ber.*, 1899, xxxii., 3109) in their experiments on the conductivity of cotarnine.

Preliminary experiments indicated that similar results are given by hydrastinine.

Discussion.

Mr. Baly said that an interesting comparison could be drawn between these absorption spectra of cotarnine compounds and those obtained by Hartley and Dobbie with derivatives of *o*-oxycarbanil. In the latter case, the lactam esters correspond to the derivatives from the ammonium hydroxide form of cotarnine, and the lactim esters to the derivatives from the carbinol form. The absorption spectra of the lactim esters of *o*-oxycarbanil and of the ammonium hydroxide form of cotarnine, both have more general absorption with the absorption band nearer to the visible region than in the case of the spectra of the lactim esters of *o*-oxycarbanil and the carbinol form of cotarnine. This contrast appears to be the opposite of that observed in the keto and enolic forms of carbon compounds.

Dr. Orton asked whether the addition of a small quantity of alcohol to the ethereal solution of cotarnine, in which the alkaloid was present in the carbinol (or pseudo ammonium) form, effected a *complete* conversion of the carbinol into the true ammonium base; or was, on the other hand, a point of equilibrium reached which was only displaced by addition of a further quantity of alcohol? As the presence of small quantities of bases such as piperidine has such a marked influence on similar isomeric changes, preventing the change of a non-basic into a basic substance, and facilitating the reverse process, it would be of interest to know whether any similar observations on the transformation of cotarnine under the influence of alcohol has been made.

In reply to Mr. Baly, Prof. Dobbie stated that no such general relation between the absorption spectra of lactams and lactims, as seemed to be implied in the question, had been established.

With reference to Dr. Orton's question, he stated that the amount of change produced by sodium hydroxide in an aqueous solution of cotarnine was found to be proportional to the quantity of caustic alkali added, when the solution was examined immediately after the addition of this reagent. The effect of time on the alkaline solution had not yet been fully investigated.

*49. "*Decomposition of Mercurous Nitrite by Heat.*" By P. C. Ray and J. N. Sen.

When mercurous nitrite was decomposed by heat in a tube connected with a Sprengel pump, nitric oxide escaped mixed with very little nitrogen peroxide, crystals of mercurous nitrate were projected across the upper and cooler part of the tube, just over the decomposing salt, a very little metallic mercury and its basic nitrate were deposited at the sides, whilst a small quantity of amorphous, orange-coloured mercuric oxide was left in the place of the decomposed nitrite. Except when the greater portion of the nitrate which had formed at first had been decomposed by heating more strongly, the average amount of nitric oxide produced corresponded with only 3·3 out of the 5·7 per cent of nitrogen contained in the nitrite.

The production of mercurous nitrate was evidently due to interaction between nitrogen peroxide and mercury vapour, nitric oxide being the other product. In decomposing, the mercurous nitrite behaves partly as if it had a non-oxylic constitution in yielding mercury and nitrogen peroxide, and partly as if it had an oxylic constitution in giving rise to mercuric oxide and nitric oxide.

Discussion.

Dr. Divers said that the authors' observation of the conversion into crystals of mercurous nitrate of the nitric peroxide and mercury vapour coming from the mercurous nitrite was very interesting, and recalled the production of crystals of mercurous chloride from a mixture of mercury vapour, air, and hydrochloride acid, which occurred in the manufacture of that substance in the old Japanese way. It also strikingly confirmed, as the authors had pointed out, the accuracy of the account of the decomposition of silver nitrite given by Shimidzu and himself years ago. He considered the authors to be mistaken as to the origin of the small quantity of mercuric oxide which was always produced. That this formed just where the mercurous nitrite had lain was not that the nitrite had directly decomposed into mercuric and nitric oxides, but that, by the use of a small flame as applied, this spot was the only part of the tube sufficiently hot to bring about the well-known decomposition into this oxide of the mercurous nitrate which was forming out of the gas and vapour, equally and as much here as in the upper and cooler part of the tube.

50. "*The Action of Nitrogen Tetroxide on Pyridine.*" By J. F. Spencer.

In attempting to nitrate pyridine, the author studied the action of nitrogen tetroxide on this base, and although nitropyridine was not isolated an isomeride was produced. The nitrogen tetroxide, which was prepared by the direct combination of nitric oxide and oxygen, was employed either in the gaseous form or as a liquid at low temperatures; but these variations of the experimental conditions did not materially affect the course of the reaction, which gave rise to the same product whether the base was treated alone or in the presence of various solvents.

The first product is an unstable, white crystalline compound which was shown by analysis to be an additive compound of pyridine and nitrogen tetroxide. The further action of the latter reagent led to the production of a solid, black substance, which, when treated with water, entirely dissolved, yielding a brownish-red solution; this solution, on further dilution, gave a yellow, amorphous deposit (i.) amounting to about 4 per cent of the pyridine taken. The filtrates, when rendered alkaline, furnished 70 per cent of unaltered pyridine, but no other basic substance. If, however, the alkaline solution was acidified, it gave a purplish-brown precipitate (ii.), the composition of which was not determined.

(i.). The yellow product, which is insoluble in all the ordinary organic solvents except pyridine, dissolves in mineral acids or aqueous alkalis, forming deep red solutions; when rapidly heated, it decomposes explosively at 234°; on distillation with zinc dust, it yields pyridine:—

0·1986 gave 0·3530 CO_2 and 0·0568 H_2O. C = 48·66, H = 3·19.

0·0691 gave 13·44 c.c. moist nitrogen at 13° and 764·6 m.m. N = 22·77.

$C_5H_4O_2N_2$ requires C = 48·38, H = 3·22, N = 22·58 per cent.

These results were confirmed by many additional analyses. The hydrochloric acid solution of this substance yielded a platinichloride containing 13·53 per cent Pt. Calculating the molecular weight of the polymeride from this result, the value 521 is obtained; this corresponds with the molecular formula $(C_5H_4O_2N_2)_4$, which has a molecular weight 496. All attempts to depolymerise this substance failed; mild reducing agents had no action, although tin and hydrochloric acid reduced it to a basic compound, the platinichloride of which contained 31·49 per cent Pt, whilst $(C_5NH_4\cdot NH_2)_2H_2PtCl_6$ requires 32·6 per cent Pt.

(ii.). The purple substance somewhat resembles the yellow compound, but is evidently more complex.

The unsatisfactory yields and the highly complex nature of the products have rendered it impossible to pursue this investigation.

PHYSICAL SOCIETY.

Ordinary Meeting, March 27th, 1903.

Dr. R. T. Glazebrook, F.R.S., President, in the Chair.

A paper "*On Refraction at a Cylindrical Surface*" was read by Mr. A. Whitwell.

The object of the paper is to describe and illustrate the position and form of the focal areas produced by the refraction, at a cylindrical surface, of light diverging from or converging to a point. In general, if a plane can be drawn through the point to cut the surface symmetrically, then all the light passes really or virtually through an area in this plane. In the case of the cylinder there are two such planes. One contains the radiant point and the axis of the cylinder; the other contains the point, and is normal to the axis. The equation of the locus of intersections of symmetrical rays which intersect in the first plane, for small apertures, is obtained in terms of a, the distance of the radiant point from the axis of the cylinder, r the radius, and μ the index of refraction. A set of curves is plotted for various values of a from $+\infty$ to $-\infty$, r being taken as 2 and μ as $\frac{3}{2}$. A similar equation is found for the locus of intersection of symmetrical rays which intersect in the first plane and have a maximum angle of incidence, viz., $\frac{\pi}{2}$. A set of curves for various values of a is plotted and discussed. For any particular value of a a curve from each of these two sets is the limit of the focal area, and all the light passes through the area between these curves. Two other sets of curves are plotted for various values of a, r being $= 2$ and $\mu = \frac{2}{3}$. The loci of the intersections of symmetrical rays which intersect in the second plane, when the aperture is small, are shown to be circles described about the radiant point as centre and having radii equal to $(\mu - 1)(a - r)$. In general a surface has two powers, and two powers only. Attention is called to misleading statements in two papers on this subject read before the Society recently. The authors of these papers give expressions for the power of a cylindrical or ellipsoidal surface in various directions, the expressions being deduced from a consideration of the curvature of the section of the surface by a plane containing the optic axis and inclined at various angles to the two planes considered in the present paper. These oblique powers are purely fictitious.

Prof. Everett said he had had an opportunity of studying the paper, and found the reasoning sound. He was pleased that the author had taken up the subject of focal lines rigorously, and had made no preliminary assumptions about them. The focal lines referred to in the paper were the secondary focal lines. The primary lines were only introduced near the end as caustics. Prof. Everett also indicated the cause of the false focal lines given by the author's equations. Referring to Mr. Whitwell's criticism regarding the power of an oblique section of an ellipsoidal lens, he thought that although the power was fictitious and the criticism just, there was something to be said for the advantage of using these powers in deducing the properties of lenses.

The Chairman said he agreed with Prof. Everett in his remarks concerning the rigorous treatment of the secondary focal lines.

Dr. R. A. Lehfeldt read a paper on "*The Evaluation of the Absolute Scale of Temperature.*"

The relation governing the indications of the constant-pressure thermometer is—

$$\frac{dT}{T} = \frac{dv}{v\left(1 - \frac{K_p \varepsilon}{v}\right)},$$

where T = absolute temperature, K_p = specific heat at constant pressure, and $\varepsilon = -\frac{\delta T}{\delta p}$, the Joule-Thomson effect. The relation for the constant-volume thermometer is—

$$\frac{dT}{T} = \frac{dp}{p\left(1 - \frac{K_p \varepsilon}{v} + \frac{1}{v}\frac{\partial_T \psi}{\partial p}\right)}$$

or—

$$\frac{dT}{T} = \frac{dp}{p\left(1 - \frac{K_v u}{p}\right)}$$

where $\psi = pv$ and $u = \frac{\delta T}{\delta v}$ the Joule effect. An attempt is made to work out the latter formula with the aid of existing data. It is found that $T_0 = 273{\cdot}18$ from hydrogen and $273{\cdot}2$ from nitrogen. The deviation of the constant-volume scale from the absolute scale is indicated by curves. At 100° absolute the constant-volume (hydrogen) thermometer reads 0·1 or 0·2 too low.

Prof. Callendar, in a communication sent subsequent to the meeting, said that in his paper on "The Thermodynamical Correction of the Gas Thermometer" (*Phil. Mag.*, Jan., 1903) he had incidentally mentioned that the correction for the constant-volume gas-thermometer could not be directly deduced from the Joule-Thomson cooling-effect alone, without additional data for the value of $d(pv)/dp$, unless a formula were assigned for the variation of the cooling effect with temperature; but that the value of the absolute zero could be deduced from the pressure coefficient if the Joule cooling-effect in free expansion ($dE = 0$) were known. The experimental measurement of the latter was, however, impracticable. He also wished to draw attention to his method of treating these and similar problems in terms of the diminution of volume, c, of a gas due to coaggregation of the molecules. This was a method of great practical convenience, because c was to a first approximation a function of the temperature only, whereas the capillary pressure a/v^2 of Van der Waals was a function of both temperature and pressure. The method was based on a radically distinct conception of the nature of the deviation of gases from the ideal state, as being due to the formation of temporary molecular aggregates, and not to the existence of a general molecular attraction varying as the square of the density and analogous to capillary pressure. The theory showed that different types of molecules should coaggregate in different ways, and that the law of corresponding states as usually interpreted was subject to important limitations.

Mr. Blakesley exhibited and described a Lens possessing the following properties:—

The two conjugate foci always move with the same relative rate along the axis. The size of the object always bears to the size of the image the same ratio, so that using the same object the image is always of the same size. The instrument is of one piece of glass, and constitutes a telescope whose magnifying power is the ratio which the object bears to the image in size, linear. The relation of the rate of motion of the object to that of the image is the square of the magnifying power. The following method of construction attains these ends:—Let D be the distance between the centres from which the faces are struck, and let l be the length of the instrument between the end faces. Then $l = \mu D$ where μ is the index. The quantity $l - D$ is thus fixed. Divide it into any two parts (algebraically) r_1 and $-r_2$, so that $r_1 - r_2 = l - D$, and employ these two values r_1 and r_2 as the radii of the end faces. The ratio r_1/r_2 will be the magnifying power m, which must be interpreted thus:—If the curvatures are towards the same direction, r_1 and r_2 have the same sign and m is positive. Double convexity therefore implies an inversion of the image, or a negative magnifying power.

If x be the distance of the object from the first surface encountered by the light, and y be the distance of the image from the second surface, both measured positively in the direction opposite to that of light-propagation, then—

$$ym^2 - mD = x \text{ where } m = \frac{r_1}{r_2},$$

from which—

$$\frac{dx}{dy} = m^2.$$

The fundamental condition $l = \mu D$ is that which implies an infinite focal length for a lens. This condition rules in a telescope in which the principal foci of the objective and ocular coincide. The instrument exhibited had a value +5 for the magnifying power, and was convexo-concave accordingly. Mr. Blakesley pointed out that one view to take of the instrument was to imagine the space between an objective and ocular properly situated, filled up with glass.

NOTICES OF BOOKS.

Quantitative Chemical Analysis. Adapted for Use in the Laboratories of Colleges and Schools. By FRANK CLOWES, D.Sc. (Lond.), &c., and J. BERNARD COLEMAN, A.R.C.Sc. (Dublin). Sixth Edition. London: J. and A. Churchill. 1903. Pp. 602.

THE successive editions of this book, following each other at intervals of two or three years, afford ample evidence of its value. In the present edition further alterations and improvements have been made; the section on Organic Chemistry has been revised, and processes for the determination of molecular weights by the elevation of the boiling-point, and others for the analysis of aluminium alloys have been added. New woodcuts have been introduced, as well as tables of four-figure logarithms; with regard to the latter innovation, we are not much in favour of these short tables—the present one covers but four pages; anyone in the habit of using logarithms would naturally have a book containing them on a much more extended scale.

In the section on Water Analysis, we see that the reader is referred to "Frankland's Water Analysis," or "Sutton's Volumetric Analysis," for the description and practice of the former's beautiful method for the estimation of the organic matter in water. True it is that the proper working of this method requires a good deal of skilful manipulation and constant practice, but still we think it is a pity that the authors have not given at least a description of this method, which is at once the most accurate and most valuable one used in water analysis.

Emery Grinding Machinery: a Text-book of Workshop Practice in General Tool-grinding, and the Design, Construction, and Application of the Machines Employed. By R. B. HODGSON, A.M.Inst.Mech.E. With 143 Illustrations. London: Charles Griffin and Co., Ltd. 1903. Pp. 180.

EMERY grinding has developed to a remarkable extent during recent years, and in many modern engineering shops has to all intents and purposes superseded planing and shaping machines, but the general manufacturer in metal working does not appear to have taken full advantage of the use of the emery wheel. It is to encourage the more extended use of this class of machinery that the author has compiled the volume now before us.

In these pages will be found descriptions and illustrations of a remarkably full and varied collection of emery-grinding tools and machinery.

Emery wheels can be obtained of varying degrees of coarseness according to the work to be done, the size of the grains being denoted by the number of meshes per inch of the sieve the powder passes through, from 30 to 200; finer sizes are separated and numbered according to the time they take to settle in water; for instance, ten-minutes emery means emery which will settle in ten minutes after having been shaken up with water.

The difficulties which formerly attended the making of emery wheels has now been overcome, and excellent ones are made by the vitrified process, in which the wheels are subjected to intense heat.

The usual peripheral speed for an emery wheel is 5000 feet per minute, but there are cases in which a higher or lower speed is advisable; a useful table of speeds and sizes will be found on page 22.

The book, which is divided into thirteen chapters, deals with emery grinding in all its branches, and may be fairly described as a work of a thoroughly practical character; it is well printed, and the index is an adequate one.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 11, March 16, 1903.

Solidification of Fluorine. Combination at −252·5° of Solid Fluorine and Liquid Hydrogen.—H. MOISSAN and J. DEWAR.—In a previous research the authors proved that fluorine liquefies at −187°, and at this temperature has no action on crystalline silicon, amorphous carbon, boron, and mercury. In fact, that its chemical affinities were weakened in all cases except with hydrogen, for it combines with this gas or with solid essence of terebenthine with incandescence. At this temperature in the present investigation the authors place a bulb of fluorine in liquid hydrogen, and observe it first liquefying and then solidifying to a yellow mass, which at a temperature of 20·5° absolute becomes white. Various experiments lead to the conclusion that fluorine solidifies at about 40° absolute. They also find that at 20·5° absolute this body reacts with liquid hydrogen with great violence.

Theory of Steel Tempering.—André Le Chatelier.—The author believes that the tempering of steel should be considered as the result of a strain produced by the variations of volume during the transformations, variations whose value increases with the rapidity of cooling, on account of the special coefficient of dilatation which steel possesses above the zone of transformation. The part played by carbon in the tempering is that it facilitates the lowering of the transformation zone and also it increases the intensity of the special tension which is produced above 100°. An investigation of the transformation which this characteristic tension allows is probably a means of explaining the part played by carbon and its state in steels.

Combination of Plumbic Acid with the Organic Acids.—Albert Colson.—The author obtains a new class of bodies resulting from the union of the fatty acids with normal plumbic acid, $Pb(OH)_4$, by a method which has no analogy with that of Gerhardt, the application of this latter having proved impossible in these cases.

Heat of Transformation of White Phosphorus into Red.—H. Giran.—As a result of numerous experiments the author finds that the transformation of white into red phosphorus evolves about +4 cal. This result agrees as nearly as possible with theoretical prediction. When red amorphous phosphorus is transformed into crystalline violet phosphorus, about +0·5 cal. is evolved, results which have led many chemists to believe that these two

varieties are identical. The author's results are within the limits of possible experimental error, so he cannot come to any definite conclusion on the subject.

Collargol.—M. Hanriot.—The author investigates the substance formed during the reduction of silver nitrate with ferrous sulphate.

Action of Metals on Hot Fatty Acids.—A. Hébert. The fatty acids when acted upon at a high temperature by the more oxidisable metals, are first transformed into ketones, which are decomposed in their turn, giving rise chiefly to carbon dioxide, hydrogen, and various ethylenic carbides, first giving products of degradation and then products of polymerisation of the carbides corresponding to the acids employed.

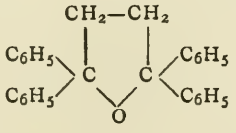
Properties of a Solution of Sodium Sulphate.—C. Marie and R. Marquis.—The authors' examination of solutions of sodium sulphate show that between the limits considered, which certainly include the transformation temperature of the salt and under the experimental conditions chosen, there is no sudden variation in the properties of the solution. It is seen, therefore, once more that there is no reason to think that in solution the salt exists with the molecules of water which make an integral part of the crystalline molecule, considered at the same temperature as the solution.

A New Method of Preparation of Plumbico-ammoniacal Chloride.—A. Seyewetz and P. Trawitz.—The authors modify Friedrich's method for the preparation of plumbico-ammoniacal chloride, by replacing the action of a current of chlorine by that of chlorine obtained from ammonium persulphate and hydrochloric acid. By this means they have no need to add ammonium chloride, as the ammonia of the persulphate serves to form the ammonium chloride necessary for the production of the double salt.

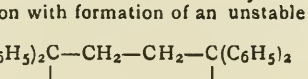
Diaminoethenic Compounds of Cadmium.—Ph. Barbier.—When a concentrated solution of diaminoethene, $C_2H_4(NH_2)_2H_2O$, is added to a moderately concentrated solution of cadmium iodide a white precipitate is formed, which re-dissolves on the addition of an excess of the reagent. The clear liquid filtered and kept for a little time deposits transparent needles having formula $CdI_2,4C_2H_4(NH_2)_2$. This compound, which the author calls cadmium tetradiaminoethene iodide, is only stable in its own mother-liquor. When water is added the crystals become opaque and crumble to a powder. From this the substance, $2CdI_2,4C_2H_4(NH_2)_2$, can be prepared.

Methylation and Condensation of Ethyl Glutaconate.—E. E. Blaise.—The methylation of ethyl glutaconate under the simplest conditions, *i.e.*, at 0°, gives a dimethylglutaconic ether boiling at 130° under 14 m.m. The author investigates this reaction, which is of a very complex nature.

Tetraphenylbutanediol and its Products of Dehydration.—Amand Valeur.—The dehydration of tetraphenylbutanediol takes place between the two tertiary alcoholic functions giving rise to tetraphenyl-tetrahydrofurfurane—



This radicle opens under the action of hydrochloric acid in acetic solution with formation of an unstable chlorated alcohol—



which by loss of HCl and H_2O gives rise to the tetraphenylbutadiene—

$$(C_6H_5)_2C=CH-CH=C(C_6H_5)_2.$$

New Derivatives of Acylcyanacetic Ethers.—Ch. Schmitt.—The author prepares a series of derivatives of acylcyanacetic ethers by the action of acid chlorides on the silver salts of the ethers.

MISCELLANEOUS.

Estimation of Molybdic Acid by Reduction by means of Hydriodic Acid.—F. A. Gooch and O. S. Pulman.—This method consists of reducing molybdic acid to the state of Mo_2O_3 by means of hydriodic acid. Practically we proceed in the following manner:—We treat 0·3 to 0·5 grm. of molybdate with at least 20 c.c. of hydrochloric acid of 1·20 density, and 0·2 to 0·6 grm. of potassic iodide in a vessel of 150 c.c. capacity, covering it with a clock-glass to prevent any loss. Heat to boiling until the original volume of the solution, 40—60 c.c., is reduced to 25 c.c., then dilute to 125 c.c., cool, and transfer to a Drechsel flask fitted laterally with a Will-Varrentrapp tube, which must be filled with a solution of potassic iodide. We then add 0·5 grm. of sulphate of manganese and an excess of titrated solution of permanganate. Finally, we run into the solution a known volume of a solution of arsenious acid. After adding a little tartaric acid, to prevent the precipitation of molybdenum, we neutralise the excess of acid by means of bicarbonate of potassium, and titrate the excess of arsenious acid with a solution of iodine. The amount of permanganate used, lessened by the quantity of arsenious acid added, and increased by the volume of iodine solution used, gives the amount of molybdic acid present in the solution. The results obtained are very accurate.—*Zeit. Anorg. Ch.*, vol. xxix., p. 353.

Yellow Sub-oxide of Copper.—Max Groger.—This sub-oxide is prepared in the following manner:—Ten grms. of pure dry cuprous chloride and 50 grms. of pure sodic chloride are dissolved in 250 c.c. of warm boiled water. We then pour this mixture, drop by drop, by means of a funnel and a tap, stirring vigorously all the while, into a solution in a vessel of 600 c.c. capacity, consisting of 10 grms. of caustic soda, 10 grms. of seignette salt, and 150 c.c. water. The vessel is filled completely with water, stoppered with an indiarubber stopper, and well shaken up with the help of a machine. In this manner we obtain a bright orange-yellow powder, which must be washed with a solution of seignette salt until the filtrate no longer contains a trace of sodic chloride, then with cooled boiled water. The precipitate is dried on a porous plate, then at the ordinary temperature in the air. The precipitate then has a brownish orange-yellow colour. It is not a true hydrated protoxide, but a cuprous oxide retaining a small quantity of water. The author found variable quantities of water from 2·54 to 0·95 per cent. This yellow sub-oxide remains unchanged, when it is dry, in contact with air; when in contact with water oxidation only takes place with difficulty, and probably this is only due to the presence of a trace of alkali. This trace of alkali would have the effect of dissolving a small quantity of the sub-oxide, which, in contact with the air, is transformed into hydrated cupric oxide. The solution of seignette salt reacts on the sub-oxide in contact with the air, giving a blue solution. The crystallised red sub-oxide of copper, obtained by precipitation from Fehling's solution by means of dextrose, is also transformed into the black cupric hydrate on contact with dilute soda solution in the presence of air; but this transformation is much slower than in the case of the yellow sub-oxide. These two modifications are comparable, through their properties, with the two oxides of mercury, the red and the yellow.—*Zeit. Anorg. Ch.*, vol. xxxi., p. 326.

School Board for London.—The Annual Exhibition of Scholars' work from the Board Schools of London will be held at the Examination Hall, Victoria Embankment (adjoining Waterloo Bridge), on Saturday May 9th, 1903, and on the following Monday, Tuesday, and Wednesday (May 11th, 12th, and 13th). The Exhibition will be opened by Lord Reay, G.C.S.I., G.C.I.E. (Chairman of the Board), at 12 o'clock, noon, and will include specimens of Drawings, Colour-work, Modelling, Science Apparatus, Wood-carving, Metal-work, Needlework, Infants' work, Cookery, Laundry-work, and Housewifery from the Day and Evening Schools, and also work from the Schools for the Blind, Deaf, Special Instruction, Truant, and Industrial Schools. Arrangements will also be made for various classes at work in practical Cookery, Laundry-work, &c., during the day-time; and Gymnastics, Dramatic, Literature, &c., in the evenings.

Ethylbenzylaniline.—G. Schultz and E. Bosch.—The authors have made a study of ethylbenzylaniline which was discovered a long while ago, and serves for the preparation of colouring materials, but of which the properties are very little known. This base, which was obtained from the "Farbwerke Höchst." distils at 275—298° at the ordinary pressure, decomposing at 185—186·5° under 22 m.m.; its density is 1·034 at 18·5°. Its picrate fuses at 114°. By nitrating ethylbenzylaniline in cooled sulphuric solution, by means of a mixture of nitric and sulphuric acids also cooled in such a manner that the temperature never exceeds 5°, two nitrated derivatives are obtained, of which one, in orange-yellow prisms, fuses at 69°, and the other, in citron yellow rhombic crystals, at 67°; these two bodies are separated, one from the other, by crystallisation in alcohol. The body fusible at 67°, which only occurs in small quantities, has not yet been examined very closely, but the one fusing at 69° is a mononitroethylbenzylaniline, of which the hydrochlorate fuses at 186° and the picrate at 131°. By oxidation it gives *m*-nitrobenzoïc acid, and by reduction *m*-amido-ethylbenzylaniline, an almost colourless oil distilling at 261—262° under 57 to 58 m.m. pressure. Its hydrochlorate fuses at 188—190°. The nitroso-ethylbenzylaniline was prepared from ethylbenzylaniline by the ordinary method. It crystallises in ether, and fuses at 62°. When boiled with hydrochloric acid we obtain a compound which crystallises in needles and fuses at 216°, and, at the same time, a large quantity of benzaldehyde and an oily base. Nitrosoethylbenzylaniline, when reduced by means of zinc powder, gives *p*-amidoethylbenzylaniline, a thick, nearly colourless oil, which distils without decomposition at 225° under 21 m.m. Its hydrochlorate is very hygroscopic; its oxalate is a white crystalline powder, fusible at 168—169°; its benzoylic derivative occurs in needles, fusible at 124°.—*Berichte*, vol. xxxv, p. 1292.

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AND

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THE CHEMICAL NEWS.

Vol. LXXXVII., No. 2264.

TENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1902.*

By F. W. CLARKE.

During 1902 there has been a fair amount of activity in the determination of atomic weights, and some of the work published is highly important. One new metal (radium) appears as a definite element for the first time, taking its proper place in the periodic system as a member of the calcium, strontium, barium group. The recorded investigations are summarised below. The work on iodine, calcium, selenium, lanthanum, and uranium is especially worthy of notice.

Iodine.

In order to establish more exactly the relative positions of tellurium and iodine under the periodic law, Ladenburg has re-determined the atomic weight of the latter element (*Ber.*, xxxv., 2275). His process consisted in transforming silver iodide to silver chloride, by heating in chlorine, and a preliminary series of experiments gave the following results. All weights were reduced to a vacuum, and the calculations are based upon O = 16.

Weight AgI.	Weight AgCl.	Atomic weight I.
31·2558	19·0817	126 93
33·7357	20·5930	126·96
49·88229	30·4525	126·94
47·8830	29·2262	126 98
60·1435	36·7154	126·95
41·3649	25·2448	127·01
50·8916	31·0664	126·95
41·3233	25·2200	126·98
80·8139	49·3181	127·02
89·5071	54·6367	126·96
	Mean	126·97

This value is notably higher than that given by Stas, 126·85, and therefore additional determinations were necessary. Three experiments, conducted with the utmost care and with all needful precautions, gave as follows:—

Weight AgI.	Weight AgCl.	Atomic weight I.
62·6608	38·2496	126·957
63·8351	38·9656	126 961
74·7516	45·6288	126·963
	Mean	126·960

This result serves to vindicate the preliminary series, but the cause of the difference from Stas's value is yet to seek. One careful experiment by Stas's method, the synthesis of silver iodide, was made by Ladenburg, whose data, with all corrections applied, are these:—

50·3147 Ag gave 109·4608 AgI. Hence I = 126·87.

Here Stas is corroborated, and the difference is evidently due to the different methods. Ladenburg regards the synthesis of the iodide from silver as attended by much much greater errors than affect the other method, and says that their tendency is to lower the apparent atomic weight of iodine. The new data, therefore, are entitled to very respectful consideration.

Two syntheses of silver iodide are also given by Scott, incidentally to his research upon tellurium (*Proc. Chem. Soc.*, xviii., 112, May 7, 1902). The data are subjoined, and represent reductions to a vacuum, and calculations based upon O = 16 and Ag = 107·93.

Weight Ag.	Weight AgI.	Atomic weight I.
4·6240	10·0634	126 96
6·39978	13·92913	126 98

Here, again, there is a variation from Stas, and an agreement with the higher value obtained by Ladenburg. It seems clear that the atomic weight of iodine should be most carefully scrutinised.

Calcium.

An important preliminary notice by Richards describes a number of experiments upon the atomic weight of calcium (*Journ. Am. Chem. Soc.*, xxiv., 374). The compound studied was the chloride, and the results, reduced to a vacuum, were as follows (O = 16, Cl = 35·455):—

Weight $CaCl_2$.	Weight AgCl.	Atomic weight.
1·56454	4·0409	40·121
3·57630	9·2361	40·130
3·59281	9·2788	40·129
5·00880	12·9364	40·124
9·00246	23·2506	40·125
	Mean	40·126

Still another paper upon this subject, by Hinrichsen (*Zeit. Phys. Chem.*, xl., 746), is supplementary to the memoir which he published in 1901 (*Ibid.*, xxxix., 311). Transparent calcite from Russia was reduced to lime by ignition. After reduction to a vacuum and correction for known impurities in the original material, the subjoined data were obtained.

Weight $CaCO_3$.	Weight CaO.	Atomic weight.
31·20762	17·49526	40·139
22·00588	12·33642	40·136

The value found in 1901 was Ca = 40·142. These figures harmonise with those of Richards, and prove that the formerly accepted number, Ca = 40, is too low.

Selenium.

Atomic weight re-determined by Julius Meyer (*Zeit. Anorg. Chem.*, xxxi., 391; *Ber.*, xxxv., 1591). Silver selenite, scrupulously pure, was analysed electrolytically. The data, with all weights reduced to a vacuum, are as follows:—

Weight Ag_2SeO_3.	Weight Ag.	Per cent Ag.	Atomic weight.
0·5152	0·3241	62·907	79·28
0·5237	0 3295	62·915	79·24
1·8793	1·1826	62·928	79·17
2·1460	1·3503	62·922	79·20
1·6964	1·0672	62·910	79·27
	Mean..		79·23

From the sum of the weights, corrected for a trace of silver which remained in solution after electrolysis, the final result becomes—

Se = 79·21.

This figure is nearly in accord with Lenher's determination, but notably higher than that obtained by Pettersson and Ekman.

Tellurium.

Guthier (*Liebig's Ann. Chem.*, cccxx., 52), in order to determine the atomic weight of tellurium, has studied telluric acid and tellurium dioxide. His analyses depended upon the precipitation of tellurium by hydrazine hydrate, and special precautions were taken to avoid any oxidation of the precipitated metal. The latter was found to be extremely oxidisable. First, two direct determinations were made of water in telluric acid, as follows:—

* *Journal of the American Chemical Society*, xxv., No. 3.

Weight H_6TeO_6.	Weight H_2O.	Per cent H_2O.	Atomic weight.
0·4937	0·1162	23·54	127·60
0·9910	0·2335	23·56	127·70
		Mean	127·65

All weights were reduced to a vacuum, and calculations were based upon O = 16 and H = 1·008.

Secondly, Guthier gives six determinations of tellurium in telluric acid, after several fractional crystallisations of the latter. Three separate fractions were studied, with duplicate determinations on each. The data are given below:—

Weight H_6TeO_6.	Weight Te.	Per cent Te.	Atomic weight.
0·9380	0·5204	55·48	127·20
0·4963	0·2754	55·49	127·25
1·0485	0·5829	55·60	127·80
0·8865	0·4915	55·44	127·00
0·4339	0·2411	55·56	127·60
0·3492	0·1937	55·48	127·34
		Mean	127·365

From tellurium dioxide, similarly reduced, the following data were obtained:—

Weight TeO_2.	Weight Te.	Per cent Te.	Atomic weight.
0·1662	0·13287	79·94	127·50
0·3136	0·2507	79·94	127·50
0·2799	0·2238	79·95	127·60
		Mean..	127·53

The average of the three series of determinations is—

Te = 127·51.

The low results of the second series are probably ascribable to traces of mother-liquor retained in some crystals of the telluric acid.

A preliminary notice upon the atomic weight of tellurium has also been published by Scott (*Proc. Chem. Soc.*, xviii., 112, May 7, 1902). The substances studied were trimethyl tellurium iodide, $Te(CH_3)_3I$, and the corresponding bromide. Analyses of the iodide were as follows:—

Weight $Te(CH_3)_3I$.	Weight AgI.	Atomic weight.
1·7461	1·3688	127·70
6·6425	5·20575	127·66
8·0628	6·3181	127·69

The bromide was titrated with silver solution, and gave these results:—

Weight $Te(CH_3)_3Br$.	Weight Ag.	Atomic weight.
2·4294	1·0373	127·77
6·8424	2·9201	127·78

The second sample of bromide was not so pure as the first. Rejecting it, the mean of the other four determinations gives Te = 127·70. The mean of all five is 127·74. All weights are reduced to a vacuum, and the antecedent values are O = 16, C = 12·00, H = 1·0075, I = 126·85, Br = 79·95, Ag = 107·93.

Lanthanum.

The determinations of atomic weight by Jones were made upon material of remarkable purity (*Am. Chem. Journ.*, xxviii., 23; CHEMICAL NEWS, 1903, lxxxvii., 169). The only contamination which could be detected with the Rowland spectroscope of the Johns Hopkins University, was a trace of cerium amounting to not more than 0·01 per cent, and probably much less. Furthermore, some of the lanthanum oxide was ignited in hydrogen in order to make sure that no oxide higher than La_2O_3 was present. The method of determination was the usual synthesis of sulphate from oxide, and careful experiments showed that under the conditions of the investigation no acid sulphate was formed. The sulphate which was finally weighed was perfectly soluble in water and absolutely neutral in reaction. Twelve determinations are given as follows. The atomic weight was calculated with O = 16 and S = 32·06.

Weight La_2O_3.	Weight $La_2(SO_4)_3$.	Atomic weight.
1·0122	1·7592	138 72
1·1268	1·9581	138 78
0·94585	1·6437	138 77
1·0675	1·8553	138·73
0 9030	1·5692	138·78
1·1273	1·9589	138·79
0·9407	1·6347	138 78
1·0455	1·8168	138·78
1·1271	1·9586	138·78
1·3074	2·2720	138 77
1·3389	2·3267	138·77
1·2012	2·0874	138·78
	Mean	138·77

An attempt was also made to use the oxalate method, but that proved to be unsatisfactory.

A second memoir upon lanthanum, by Brauner and Pavlíček (*Journ. Chem. Soc.*, lxxxi., 1243; also CHEMICAL NEWS, 1903, vol. lxxxvii., p. 49, *et seq.*), is even more elaborate than that of Jones. The method of determination was the same in both cases, but there are many differences of detail. The Bohemian authors find a serious difficulty in the presence of the acid sulphate, for which measured corrections are applied, and they also note another source of error in the hygroscopic character of $La_2(SO_4)_3$. The latter was guarded against by special precautions in weighing. The final results (omitting a preliminary series), with vacuum weights, and all corrections applied, are as follows. The calculations depend upon O = 16 and S = 32·06:—

Weight La_2O_3.	Weight $La_2(SO_4)_3$.	Atomic weight.
1·06562	1·85054	139·036
1·00694	1·74856	139·053
1·12553	1·95457	139·038
1·70276	2·95707	139 026
1·02460	1·77943	139·009
1·28650	2 23419	139·024
1·06488	1·84910	139·068
	Mean	139·036

The reverse method of determination, the ignition of sulphate to oxide, gave bad results. A series of determinations by the oxalate method gave, in mean, La = 139·07. but the individual measurements show a wide range of variation, namely, from 138·67 to 139·66. The value for the atomic weight of lanthanum derived from the sulphate syntheses is doubtless not far from the truth. The mean of the Jones and Brauner values is—

La = 139·905,

and, pending further evidence, this value may properly be adopted; although Brauner, in a later communication (*Zeit. Anorg. Chem.*, xxxiii., 317), criticises the work of Jones and argues in favour of his own determinations. Brauner insists strongly upon the presence of acid sulphate in the lanthanum sulphate studied by Jones, and also suggests that the latter overlooked the hygroscopic nature of his material. If further investigation sustains these criticisms, then the Brauner value is to be preferred.

Ytterbium.

Atomic weight re-determined by Astrid Cleve with very pure material (*Zeit. Anorg. Chem.*, xxii., 129; CHEMICAL NEWS, lxxxvi., 248). The method employed was the synthesis of the sulphate from the oxide. The data are as follows, when O = 16 and S = 32·06:—

Weight Yb_2O_3	Weight $Yb_2(SO_4)_3$.	Atomic weight.
0 7791	1·2535	173·22
0·5190	0·8353	173 05
0 4905	0·7894	173 07

These figures confirm the earlier determination by Nilson.

Uranium.

The work of Richards and Merigold upon the atomic weight of uranium is rich in details, and also in matter relative to probable sources of error (*Proc. Amer. Acad.*, xxxvii., 365; CHEMICAL NEWS, lxxxv., 177, *et seq.*). The substance finally chosen for study was uranous bromide prepared by sublimation, and scrupulously protected from the oxidising action of the air. It contained a minute quantity of sodium bromide, but the amount of this was determined and the necessary correction was applied. All weights refer to a vacuum, and the antecedent atomic weights were O=16, Ag=107·93, and Br=79·955. A preliminary series of analyses gave as follows, all corrections included.

Weight UBr_4.	Weight AgBr.	Atomic weight.
2·2058	2·9699	238·36
1·4418	1·9401	238·69
1·4050	1·8910	238·56
1·1749	1·5818	238·39
	Mean	238·50

In another and final set of experiments, the uranous bromide was titrated with known amounts of pure silver, and the precipitated silver bromide was also weighed. Hence two ratios were determined with the following results:—

Weight UBr_4.	Weight AgBr.	Atomic weight.
1·7999	2·4226	238·54
1·0662	1·4352	238·50
1·8551	2·4967	238·59
Mean		238·54

Weight UBr_4.	Weight Ag.	Atomic weight.
1·7999	1·3918	238·49
1·0662	0·8245	238·46
1·8551	1·4342	238·60
Mean		238·52
Average of all determinations.. ..		238·52
Average of last six determinations..		238·53

This result is notably lower than the usually accepted value for the atomic weight of uranium.

From Series 2 and 3 the ratio between silver and bromine may be deduced. It gives for the percentage of Ag in AgBr the number 57·447. Stas found 57·445. This agreement is eminently satisfactory.

Radium.

By many fractional crystallisations, Madame Curie (*Comptes Rendus*, cxxxv., 161; CHEM. NEWS, lxxxvi., 61) has succeeded in preparing radium chloride sufficiently pure for determinations of the atomic weight of the metal. According to Demarçay, who examined the spectrum of the material, it contained a minimum quantity of barium, incapable of exerting any appreciable influence upon the atomic weight. Three analyses were made, the chlorine being weighed as silver chloride, with the following values deduced for the atomic weight of radium.

	225·3
	225·8
	224·0
Mean..	225·0

Miscellaneous Notes.

Several papers have appeared during the year dealing with numerical relations between the atomic weights of the various elements. Three of them, by Bilecki (*Chem. Zeit.*, xxvi., 399). Marshall (*Chem. Zeit.*, xxvi., 663; CHEM. NEWS, lxxxvi., 88). and Hollins (CHEM. NEWS, lxxxvi., 147), relate to possible modifications of "Prout's law"; that is, they point out relations analogous to, but not identical with, those assumed by Prout. Schmidt (*Zeit. Anorg. Chem.*, xxxi., 147) and Stoney (*Phil. Mag.*, [6], iv., 411 and 504) discuss the connection of the atomic weights in a more purely mathematical way, and so, too, does Vincent (*Phil. Mag.*, [6], iv., 103). The logarithmic spiral of Stoney is especially suggestive. There is also an elaborate memoir by Lord Kelvin (*Phil. Mag.*, [6], iv., 177 and 281) on the "weights of atoms; and a discussion by Clarke (*Am. Chem. Journ.*, xxvii., 321; CHEM. NEWS, lxxxvi., 77) of the best method for the reduction and combination of atomic weight determinations. Ebaugh's work on the atomic weight of arsenic, which was cited in the report of your committee for 1901, has appeared in full in the *Journal of the American Chemical Society*, xxiv., 489, June, 1902.

International Committee on Atomic Weights.

This committee, which was too large for effective working, has appointed a smaller body for action. This smaller committee, consisting of F. W. Clarke, T. E. Thorpe, and Karl Seubert, has already reported, and its report has appeared in the *Journal of the American Chemical Society*, xxv., p. 1, January, 1903; *Zeit. Angew. Chemie*, xv., 1305; and the CHEMICAL NEWS, 1903, lxxxvii., p. 79). The table of atomic weights, there given, need not be repeated here.

A RE-DETERMINATION OF THE ATOMIC WEIGHT OF LANTHANUM.*

By HARRY C. JONES.

(Concluded from p. 171).

The Results.

TWELVE determinations were completed by the method just described, and the results are given below, calculated on the basis of oxygen = 16, sulphur = 32·06. These include every determination which was completed. A few determinations were lost by accident, especially in the earlier stages of the work, due to the spattering of the sulphate upon the lid of the crucible. These determinations were interrupted as soon as any spattering was discovered, and the resulting sulphate was not weighed.

	La_2O_3.	$La_2(SO_4)_3$.	$3SO_3$=240·18.	At. wt. La.
I.	1·0122	1·7592	0·7470	138·72
II.	1·1268	1·9581	0·8313	138·72
III.	0·94585	1·6437	0 69785	138 77
IV.	1·0675	1·8553	0·7878	138·73
V.	0·9030	1·5692	0 6662	138·78
VI.	1 1273	1·9589	0·8316	138·79
VII.	0·9407	1·6347	0·6940	138·78
VIII.	1·0455	1 8168	0·7713	138 78
IX.	1·1271	1·9586	0 8315	138·78
X.	1·3074	2·2720	0·9646	138 77
XI.	1·3389	2·3267	0·9878	138·77
XII.	1 2012	2·0874	0·8862	138·78

Taking the mean of the twelve determinations, we have for the atomic weight of lanthanum the value 138·77.

Attempt to Use the Oxalate Method.

An attempt was made to determine the atomic weight of lanthanum by decomposing the oxalate of lanthanum to the oxide, or by determining the oxalic acid in the oxalate by titration with a standard solution of potassium permanganate. This method had to be abandoned on account of the nature of lanthanum oxalate. It was found to be practically impossible to obtain lanthanum oxalate under conditions where it would give constant weight. The oxalate continued to lose in weight when dried for several days at 110°; it further lost in weight when dried at 150°, and still further loss in weight was sustained when it was heated to 190°. A specimen which had been dried

* From the *American Chemical Journal*, xxviii., No. 1.

for a week at 190° gave off a very considerable quantity of water when heated from 230° to 240°, showing that considerable wate. had been retained by the oxalate above 200°.

The decomposition temperature of lanthanum oxalate was then studied. The salt was placed in a glass tube closed at one end and connected at the other with a wash-bottle closed by means of a ground-glass stopper. A solution of barium hydroxide was introduced into the bottle and protected from the carbon dioxide in the air by connecting it with a second similar bottle containing a solution of sodium hydroxide. Any carbon dioxide escaping from the decomposing oxalate was thus conducted through the solution of barium hydroxide. The oxalate was found to show incipient decomposition at 250°, which became very marked at somewhat higher temperatures.

Since the oxalate continued to give off water so close to its decomposition temperature, it was not safe to completely dehydrate the salt and weigh it for the purpose of an atomic weight determination. The oxalate method for determining the atomic weight of lanthanum was, therefore, abandoned.

The result of the above investigation is, then, to show that the atomic weight of lanthanum is 138·77 on the basis of oxygen = 16.

THE MYSTERY OF RADIUM.

By Sir WILLIAM CROOKES, F.R.S.

The following letter appeared in *The Times* of April 7th:—

Sir,—Allow me to reply to your correspondents "Ignoramus" and "Physicus." I will do so as briefly as possible.

I did not nearly fill a line with ciphers to order to impress your readers. I had to do so for accuracy's sake. In England we form billions, trillions, &c., by multiplying the previous denomination by a million; in France and the United States this is effected by multiplying by a thousand. Therefore without the array of ciphers my notation would not have been understood.

"Ignoramus" says that the physical effect is mathematically proportionate to the number of molecules in the bulb; and he asks on what grounds do I assume that one unit of gas occupying a given space can produce a physical effect equal to that produced by a million units occupying the same space? My answer is that the physical effects in the rare gas will be incomparably greater than in the dense gas. Ratio has nothing to do with the matter. It is true, as your correspondents say, that air at an exhaustion of a millionth of an atmosphere is a million times less dense; but they forget that the mobility of the molecules is enormously increased; their mean free path, instead of being the ten-thousandth of a millimetre as at ordinary pressures, being lengthened to about a hundred millimetres.

Crowding does not depend so much on the number of bodies present in a given space as on the size of each body. An audience of a thousand would crowd inconveniently the theatre of the Royal Institution, but a thousand bees could fly about in the same space with no inconvenience. In the former case collisions would be almost continuous, whilst with the smaller bodies their mean free paths would be so long that the hits in a given time might be disregarded in proportion to the misses. And the same reasoning applies if we reduce the number of units present instead of diminishing their size. In spite of the fact that in air there are a trillion molecules still present at an exhaustion of a millionth, the hits in a given time are sufficiently few that we no longer have to deal with almost continuous matter, but we can contemplate, as it were, molecular actions individually. The properties which constitute gaseity are here reduced to a *minimum*, and the average molecule is free to obey its own laws with but little interference. Hence the phenomena, thermal, electrical, and mechanical, observed in "high vacua," in spite of the trillions present.

I am your obedient servant,

WILLIAM CROOKES.

London, April 4.

THE EFFECT OF CERTAIN POISONS ON INORGANIC FERMENTS.*

By HARRY C. JONES, Ph.D.,
Associate Professor of Physical Chemistry in the Johns Hopkins University.

A brief review of the work of Bredig and his pupils on inorganic ferments has already appeared in the *Johns Hopkins Hospital Bulletin*, No. 114, Septemper, 1900, p. 224. This work has been continued, and some striking relations between the inorganic ferments and certain enzymes have been established.

The inorganic ferments in question are finely divided metals, such as platinum, gold, silver, cadmium, &c. The metals are obtained in the finely divided condition by dipping bars of the metal into pure water, and passing a heavy electric current from one bar to the other through the water. The metal under these conditions is torn off in a state of such fine division that it remains suspended in the water in the form of a solution. Indeed, the metal is in such a state of division that the most powerful microscope fails to reveal any heterogeneity when a drop of the solution is brought beneath it. From this it might be concluded that these solutions of the metals are true solutions. Such, however, is not the case. True solutions freeze lower than the pure solvent, have less vapour-tension or boil higher than the pure solvent, and exert osmotic pressure. The solutions in question of the metals have none of these properties. They have the same freezing-point, the same vapour-tension or boiling-point as the pure solvent, and do not exert any osmotic pressure. To distinguish these solutions of the metals from true solutions they have been termed *pseudo-solutions* or *colloidal solutions*.

These are in no sense a new class of solutions. Examples of colloidal solutions have long been known. Solutions of starch, albumen, and the like are as truly colloidal solutions as those of the metals. The solutions of the metals, however, have certain remarkable properties which seem to resemble in many respects the properties of the organic ferments. Some of these were referred to in the earlier review. It was noted that a colloidal solution of platinum accelerates the oxidation of alcohol to acetic acid in the presence of the oxygen of the air, as well as the organic ferment *mycoderma aceti*.

Finely divided iridium decomposes calcium formate into calcium carbonate, carbon dioxide, and hydrogen in the same manner as certain bacteria.

The analogy between the action of the finely divided metals and ferments was not limited to fermentation proper, oxidation, &c.; but held also for diastatic phenomena such as the inversion of cane-sugar. The finely divided metals effected the inversion of cane-sugar in a manner which was strictly analogous to the action of invertase.

Again, hydrogen dioxide was decomposed into water and oxygen in exactly the same manner by the colloidal solutions of the metals as by the ferments in the blood.

Many relations similar to the above were pointed out by Bredig and von Berneck, in the first communication on this subject (*Zeit. Phys. Chem.*, 1899, xxxi., 258). These relations are, however, purely qualitative, and alone are entirely insufficient to establish any deep-seated connection

* From *The Johns Hopkins Hospital Bulletin*, vol. xiii., No. 134.

between the action of the finely divided metals on the one hand and organic ferments on the other.

The first investigation was a quantitative study of the action of the colloidal solutions of the metals as compared with the action of organic ferments. As this has already been reviewed, a brief reference to the conclusions reached by Bredig and von Berneck is sufficient.

It was shown in the first place that very small amounts of metal can effect the decomposition of enormous quantities of hydrogen dioxide, just as very small amounts of organic ferments can effect relatively large transformations. This analogy is, however, not necessarily very striking.

It was then shown that the finely divided metals do not enter into the reaction which they effect. The method by which this was proved was considered at sufficient length in the earlier review (*Johns Hopkins Hospital Bulletin*, 1900, 114, 225).

Substances which behave in this manner, *i.e.*, act by means of their surface alone without entering into the reaction, are known as *Catalysers*, and such reactions are termed *catalytic*. The colloidal solutions of the metals, then, act catalytically. It is also well known that enzymes act catalytically. They do not enter into the reaction as such, but act simply by contact through their surface.

This analogy between the action of the colloidal metals and the enzymes is much closer than that first referred to, and makes it probable that the relations between the two are really deep seated. There is, however, a relation far more striking than either of those considered above.

It is well known that the enzymes are very sensitive to certain substances, which, in infinitesimal quantities, may retard or entirely prevent their action. Thus, hydrocyanic acid, carbon bisulphide, hydrogen sulphide, and the like, when present in mere traces, may interfere seriously with the action of certain ferments. It has been shown that the merest trace of substances like the above may seriously interfere with the action of the colloidal solutions of the metals—may *poison* the finely divided metals. It is with this subject that the present review has to deal directly.

In their first paper certain qualitative observations were made by Bredig and von Berneck on the poisonous action of a few substances on colloidal solutions of platinum. This subject has subsequently been studied quantitatively by Bredig and Ikeda (*Zeit. Phys. Chem.*, 1901, xxxvii., 1). They have worked with colloidal solutions of platinum, and have studied the rate at which these decompose hydrogen dioxide. Solutions of certain poisons of different concentrations were added to the colloidal solution of platinum, and the rate determined at which the colloidal solution, after it had been poisoned, decomposed hydrogen dioxide.

The velocity of the decomposition was found to diminish when the poison had been added to the colloidal solution, and the amount of diminution depended upon the amount of poison present. The diminution in the velocity was worked out numerically, but the results can be seen most readily by means of curves.

Fig. 1 represents the results obtained with hydrocyanic acid as the poison. The abscissa represents the time during which the reaction has proceeded. The ordinate, log $\frac{T_0}{T}$, is really log $\frac{A}{A-x}$, in which A is the amount of the hydrogen dioxide originally present and x the amount decomposed. Without going more fully into this expression it may be stated that it is obtained by integrating the equation for a first order reaction derived from the law of mass action.

The concentration of the colloidal solution of platinum which was used, C_{Pt}, contained 0·0000103 of a grm.-atomic weight per litre. The concentration of the hydrocyanic acid which was employed, C_{CNH}, expresses the number of grm.-molecules of the acid in a litre of the solution.

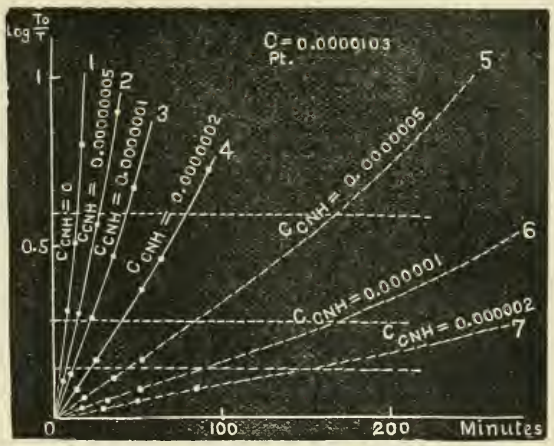


Fig. 1.—Hydrocyanic Acid.

Fig. 2.—Cyanogen Iodide.

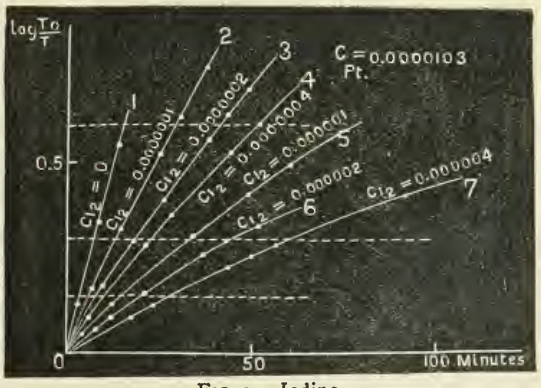


Fig. 3.—Iodine.

Curve 1 represents the reaction when no poison is present. Curves 2 to 7 represent the reactions when increasing amounts of the poison were present. Take curve 5. Here the reaction velocity has been reduced to about one-half, and this has been effected by a solution of hydrocyanic acid containing *one grm.-molecular weight in two million litres.* Such a solution contains in a litre

only 0·014 m.grm. of hydrocyanic acid, and yet is capable of diminishing the action of the colloidal platinum to one-half.

Curves 4, 3, and 2 represent decreasing amounts of the poison as expressed by the values of C. Curve 2 represents the effect of a solution of hydrocyanic acid so dilute that it contains *one grm.-molecular weight in twenty million litres* of the solution; and at such inconceivable dilutions the action of the platinum is considerably lessened.

It has been found that the action of the enzymes in the blood in decomposing hydrogen dioxide is very appreciably lessened by the addition of a solution of hydrocyanic acid containing 0·002 m.grm. in a litre.

A careful examination of the curves brings out another very interesting relation. The curves for the most dilute solutions of hydrocyanic acid are convex to the abscissa from the very origin. This means that the poison is having less and less effect as the time increases—the colloidal solution of the platinum is *recovering from the poison.*

Where the solution of the hydrocyanic acid is stronger (curves 5, 6, and 7) the curve is at first concave to the abscissa, and becomes convex only after a much longer time has elapsed. While the curve is concave to the abscissa the action of the poison is increasing, and the platinum begins to recover from the effect of the poison only after a much longer interval of time.

Similarly, it has been shown that the enzymes in the blood and ferments can recover from the poisonous action of minute traces of hydrocyanic acid.

It is pointed out that both of these effects are probably due to the oxidation of the hydrocyanic acid in the solution.

A more violent poison than hydrocyanic acid is cyanogen iodide. The results obtained with this substance are shown in Fig. 2.

Curve 1 represents the reaction when none of the poison is present. Curves 2 to 11 represent the results with increasing amounts of the poison. When the concentration of the poison is such that a *grm.-molecular weight is contained in forty million litres* of the solution, the action of the platinum is very appreciably diminished. The diminution in the velocity of the reaction is increased as the concentration of the poison becomes greater and greater. When the poison has acquired a concentration of a grm.-molecular weight in about thirteen million litres, the velocity of the reaction is reduced to one-half.

These curves show that the colloidal solution of platinum can *recover* also from the poisonous action of cyanogen iodide, provided the poison is not too concentrated. If the dilution is greater than a grm.-molecular weight in a million litres (curves 2 to 6) the platinum can recover in part from the effect of the poison, as is shown by the curves becoming convex to the abscissa. If the concentration is greater than one million litres the curves remain concave to the abscissa, which means that the colloidal solution cannot recover from the effect of the poison.

It should be noted that cyanogen iodide is one of the strongest poisons toward blood and protoplasm in general.

The effect of one other poison will be taken up, since it represents the case where the colloidal solution cannot recover at all from the poisonous effects. This poison is *iodine.* The results obtained are shown in Fig. 3. From what has already been said concerning the curves in Figs. 1 and 2, the curves in Fig. 3 are self-explanatory. It will be observed that none of the curves become convex to the abscissa, which means that no matter how dilute the poison, provided that it is sufficiently concentrated to have any appreciable effect, the platinum cannot recover from its influence.

The curves show also that iodine is a powerful poison on the colloidal metal, and it is known to be an intense blood poison.

In a manner exactly analogous to that described above, Bredig and Ikeda have studied the poisonous action of about thirty substances on colloidal solutions of platinum. The strongest poisons in addition to those described above are mercuric chloride, hydrogen sulphide, sodium thiosulphate, carbon monoxide, phosphorus, phosphine, arsine, mercuric cyanide, and carbon bisulphide. From the effect of some of these substances the platinum was able to recover, as in the cases of hydrocyanic acid and cyanogen iodide, while the action of others remained permanent as with iodine. Among the substances which are less poisonous to the platinum are aniline, hydroxylamine, bromine, hydrochloric acid, oxalic acid, amyl nitrite, arsenious acid, sodium sulphite, and ammonium chloride.

The weak poisons are;—Phosphorous acid, sodium nitrite, nitrous acid, pyrogallol, nitrobenzene, ammonium fluoride, &c.

A few substances were found to be nearly neutral in their action, such as potassium chlorate, ethyl alcohol, amyl alcohol, ether, glycerol, oil of turpentine, and chloroform; while formic acid, hydrazine, and dilute nitric acid increased the activity of the colloidal platinum in breaking down hydrogen dioxide.

At the close of their paper Bredig and Ikeda compared the action of a number of substances on the power of colloidal platinum on the one hand, and of blood on the other, to break down hydrogen dioxide. Their results are given in the following table:—

Retardation of the Catalytic Decomposition of H_2O_2.

	By Blood. Catalysis—	By Colloida Platinum. Catalysis—
Hydrogen Sulphide	No catalysis.	Very strongly retarded.
Iodine	Very strongly retarded.	Very strongly retarded.
Mercuric Chloride .	Almost entirely prevented.	Very strongly retarded.
Mercuric Cyanide .	Very considerably weakened.	Very strongly retarded.
Hydrocyanic Acid .	Very considerably weakened.	Very strongly retarded.
Hydroxylamine ..	Entirely prevented.	Strongly retarded.
Amyl Nitrate ..	Strongly retarded.	Strongly retarded.
Nitrobenzene ..	Appreciably weakened.	Slightly weakened.
Pyrogallol	Not lessened.	Slightly lessened.
Arsenious Acid ..	Inappreciably lessened.	Slightly lessened.
Potassium Chlorate	Slightly decreased.	Not decreased.
Aniline	Strongly increased.	Considerably decreased.

That there is a general agreement between the action of poisons on organic and inorganic ferments is unmistakable from the above results. Certain differences, however, manifest themselves as in the case of aniline, and it is impossible to say at present what these mean.

An impartial examination, however, of all the evidence bearing upon the relation between organic and inorganic ferments will certainly lead to the conclusion that these analogies are not accidental. The state of mind of Bredig on this whole problem can be seen best by quoting the following paragraphs from his monograph on this subject:—

"All these facts point to an unmistakable analogy between the contact actions in the inorganic world and the actions of ferments in the organic world. As in the case of my colloidal catalysers, we are dealing with reactions in which enormously developed surfaces are involved, so is it probable that the same condition obtains in the actions of ferments, enzymes, blood corpuscles, and oxidising and catalysing organic substances. We see,

therefore, that the organism develops its enormous surfaces in the tissues and colloidal ferments not only because it requires osmotic processes, but on account of the very great catalytic activity of such surfaces. If, as Boltzmann says, the war for existence which living matter must wage is a war about free energy, certainly, of all the forms of free energy the *free energy of surface* is the most important for the organism.

"In conclusion, I need scarcely state that I do not maintain that there is any mysterious identity between the metals and the enzymes. But without exaggerating the overwhelmingly large number of analogies, we are compelled to regard the colloidal solutions of the metals, in many relations at least, *as inorganic models of the organic enzymes*."

The author would refer the action of the colloidal solutions of the metals, the enzymes, and catalysis generally to the *surface energy* possessed by these substances. We are thus led one step nearer to the solution of the nature of catalysis, which underlies so many of the processes of living as well as dead matter.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

ANNUAL GENERAL MEETING, *March 25th*, 1903.

Prof. J. EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

DR. L. T. THORNE and Dr. K. J. P. ORTON were appointed scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year. The PRESIDENT then presented the following Report on the state of the Society during the past twelve months:—

Report of the Council.

The Council have the satisfaction of announcing that the numerical strength of the Society, which, on March 26th, 1902, was 2416 is now 2471, the highest number yet reached. Since the last Annual General Meeting, 130 Fellows have been elected and 6 have been reinstated by the Council, making a gross total of 2552. Of these, 27 have been removed for non-payment of two subscriptions, 33 have withdrawn, and 21 have died, making 55 the net increase in the number of Fellows.

By the death of Professor J. Wislicenus, F.R.S., the number of Foreign Fellows has been reduced to 31.

The following Fellows have died:—Sir F. A. Abel, Bart., F.R.S.; Dr. C. M. Aikman; F. B. Benger; C. R. Blackett; Prof. G. Bischoff; Dr. E. Demarçay; W. C. Forsyth; T. E. Gee; Dr. J. H. Gladstone, F.R.S.; G. Griffith; Prof. J. J. Hummel; R. Jackson; W. I. Macadam; J. Moss; J. Robbins; Sir W. C. Roberts-Austen, K.C.B., F.R.S.; Dr. E. Schunck, F.R.S.: J. Sim; W. H. Stanger; E. Truman; M. Zingler.

The scientific work of the Society during the past session abundantly testifies to its continued activity. Since the last Annual General Meeting, 189 scientific communications have been made to the Society, 118 of which have already been published in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The *Transactions* for 1902 contains 160 memoirs, occupying 1604 pages, whilst the volume for the preceding year contains 146 memoirs which occupy 1411 pages. In addition, the volume for 1902 contains the Raoult Memorial Lecture.

The *Journal* for 1902 contains also 3854 abstracts of papers, published mainly in foreign journals, which extend to 1564 pages. These abstracts may be classified as follows:—

PART I.	Pages.	No. of Abstracts.
Organic Chemistry	852	1632
PART II.		
General and Physical Chemistry		409
Inorganic Chemistry		428
Mineralogical Chemistry		154
Physiological Chemistry		421
Chemistry of Vegetable Physiology and Agriculture		281
Analytical Chemistry		529
	712	2222
Total in Parts I. and II. ..	1564	3854

The Council desires to offer the congratulations of the Society to Professor G. D. Liveing, F.R.S., and to Mr. J. G. Hepburn, who this year reach the Fiftieth Anniversary of their election as Fellows.

The Society has to lament the death of one distinguished Foreign Fellow, Professor J. Wislicenus, F.R.S., and of twenty-one Fellows, amongst whom are two Past Presidents, Sir F. A. Abel, Bart., F.R.S., and Dr. J. H. Gladstone, F.R.S., who had been Fellows for the long period of fifty-five years; other notable names are those of Sir W. C. Roberts-Austen, K.C.B., F.R.S., Professor J. J. Hummel, and Dr. E. Schunck, F.R.S. Obituary notices of these will appear in the Journal.

The Raoult Memorial Lecture was delivered before a large audience in the Theatre of the Royal Institution (the use of which was kindly granted for the occasion by the Managers) on March 26th, 1902, by Prof. J. H. van't Hoff, F.R.S.

The Council are glad to be able to announce that Prof. W. H. Perkin, F.R.S., has undertaken to deliver the Wislicenus Memorial Lecture towards the end of the present year.

The Society, in conjunction with the Royal Society and the other Scientific Societies having rooms in Burlington House, arranged for the decoration and illumination of the Building on the occasion of the Coronation of the King.

The plan of holding the Ordinary Meetings of the Society alternately on Wednesdays, at 5.30 p.m., and on Thursdays, at 8 p.m., which was tried for the first time last session, proved so satisfactory that the Council determined to continue the practice during the present session. Both sets of meetings have been equally well attended, and the meetings held on Wednesdays appear, in particular, to suit the convenience of Fellows resident at distance from London.

The Joint International Committee on Atomic Weights, on which the Society is represented by Prof. Thorpe, has issued its first Report. This report, which includes a new table of atomic weights, has been printed in full, both in the *Journal* and the *Proceedings*.

The Society having been invited by the Organising Commitee of the Fifth International Congress of Applied Chemistry to co-operate with other societies in this country in securing a proper representation of English chemistry, the Council, in June last, appointed a committee to take action in the matter, and have nominated, as its Delegates to represent the Society at the meeting of the Congress in Berlin in June next, the following Fellows:—Prof. W. A. Tilden, Prof. W. R. Dunstan, Prof. W. H. Perkin, and Dr. A. Scott.

A petition has been addressed to the Council requesting them to consider the desirability of limiting the period of service of the Honorary Secretaries and of the Foreign Secretary. The Council having fully considered the matter, passed, *nem. con.*, a resolution stating that whilst the tenure of office should not be indefinitely extended, it was not expedient to fix a definite term of years to the tenure of these offices.

The rapid growth of the Library rendered it imperative

that additional accommodation for its extension should be obtained at once. This has been accomplished by utilising for that purpose some of the rooms of the basement, and plans are at present under consideration by which storage accommodation there for the less used books may allow of the normal growth of the Library for another ten or twelve years without its being unduly cramped. This, along with the constantly increasing amount of work entailed by the continuous growth and prosperity of the Society, rendered necessary the rearrangement of the duties of the Staff. After careful consideration, the Council decided to separate the duties of Assistant Secretary from those of the Librarian and Curator, Mr. Steele retaining the latter, whilst Mr. S. E. Carr has been appointed Assistant Secretary.

A complete card catalogue of the Library has now been made, and the new Catalogue, arranged both according to authors and subjects, was issued at the beginning of the present year at the price of half-a-crown. The Library continues to be increasingly used by the Fellows. 925 books were borrowed during the year as against 873 in the previous year. The additions to the Library comprised 64 books, 338 volumes of periodicals, and 23 pamphlets, the corresponding numbers of which in the year before were 153, 441, and 33 respectively. Of the books, 48 have been presented to the Society.

Grants amounting in all to £230 have been made from the Research Fund.

The Council here desires to place on record its high appreciation of the conspicuous services of Prof. Dunstan, who now retires from the post of Honorary Secretary which he has held with such advantage to the Society, and who, for the last ten years, has given unsparingly both his time and his energy to the promotion of its highest interests. As one of the Vice-Presidents, the Council hope to have him among them for some time to come.

Another material change in the administrative officers of the Society comes into force with the nomination of the Treasurer, Prof. Tilden, to the highest office in the Society, that of President. The Council acknowledges with gratitude the skill and foresight with which, for the last four years, he has controlled the finances of the Society, and it is largely owing to his management, as well as to the ever increasing prosperity of the Society, that the Council has been able to introduce several important reforms and re-arrangements. These are alluded to elsewhere in this report, and it is hoped that they will greatly increase the usefulness of the Society.

Prof. W. P. Wynne found it necessary, to the great regret of the Council, to resign the post of Editor of the *Journal* which he has held for the last four years with such credit to the Society, but kindly consented to act as Editor until the end of 1902, when he was succeeded by Dr. G. T. Morgan, who, in addition to editing the *Journal*, now edits the *Proceedings* of the Society.

Report of the Treasurer.

The Treasurer, in presenting the balance sheet for the year, stated that the net income was £6212 5s. 1d., whilst the expenses had been £5384 18s., leaving a surplus of £827 7s. 1d., which was about one hundred pounds less than the surplus income in 1902. This was due to several causes, namely, the increase of nearly £380 in the cost of the *Journal* and *Proceedings*, the additions to the item of salaries and wages, and the expenses on account of the Collective Index. Whilst, therefore, the present surplus is satisfactory in that it exceeds the amount paid into the account in the form of compositions and admission fees, all these three forms of expenditure will still require careful watching. Three years ago, at the end of his first year as Treasurer, he made an appeal to authors of papers with reference to the preparation of copy for the printers, and he could not help thinking that in the near future more stringent regulations in regard both to the state of the manuscript and the dimensions of papers would have to be imposed with the object of keeping the cost of printing within the means at the disposal of the Society. The Abstracts of foreign and other journals are now indispensable, but, notwithstanding the care exercised by the Sub-Editor, to whom the Society is greatly indebted, and the very moderate remuneration of the excellent body of Abstractors, the cost of their preparation is very heavy.

The amount which will appear in the next balance sheet under the heads of salaries and wages will be somewhat larger, inasmuch as the increase will represent that for an entire year instead of only half a year as on the present occasion. The total cost of the last two volumes of the General Index was £1740, whilst the expenditure on the volume which is in course of preparation has, up to the present, been £204. The greater part of the cost is therefore still to be met. On the other hand, the Library Catalogue is now completed, and for some years there need be no further expense in that form, although additional accommodation for the books will have to be provided immediately at an outlay which will probably approach £200.

The following tabular statement contains the chief items of income and expenditure during the past four years. The figures represent pounds, the shillings and pence being omitted. It will be seen that whilst the income of the Society is increasing the expenses are growing at nearly the same rate.

	1900.	1901.	1902.	1903.
Compositions . ..	110	282	168	299
Admission Fees ..	468	464	652	520
Subscriptions . ..	3510	3544	3712	3957
Sale of Journals ..	781	880	835	888
Dividends	444	464	476	506
Net Income	5371	5668	5844	6212
Assets	16710	17156	17807	18446
Expenses	4993	4932	4913	5384
Surplus	377	736	930	827

The Treasurer recalled with satisfaction the sale of Consols previously held by the Society in his first year of office. A serious loss was thus avoided, and, by the reinvestment of the proceeds, a slight addition was secured to the income of the Society.

The estimated values of the securities are all slightly less than at this time last year, but the further investment in May last in £1200 of Leeds Corporation Stock now brings the Assets of the Society to the respectable figure of £18,446 17s. 3d.

The Treasurer, in concluding, proposed a vote of thanks to the auditors, which was acknowledged by Dr. L. T. Thorne.

Prof. Dewar proposed a vote of thanks to the Treasurer, Secretaries, and Council. The motion was seconded by Prof. W. H. Perkin, and unanimously adopted. Prof. Dunstan responded.

The President, then delivered his Address, in which he called attention to the publication of some recent reports on progress in chemical research, and urged the publication of similar digests. He mentioned that this year would see the centenary of Dalton's statement of his atomic theory, which rose, as Nernst truly said, "by a single effort of modern science, like a phœnix from the ashes of the old Greek philosophy." He urged the study of "comparative chemistry" of inorganic compounds. There were few inquiries of greater interest than those involving inorganic isomerism, which was now either completely ignored or only slightly mentioned. Polymerism, or molecular condensation, was well known to exist in many inorganic compounds, as in the oxides of nitrogen, vanadium, niobium, and tantalum. Silicon showed a great analogy to carbon, and it was highly probable that some of the native silicates were benzenoid combinations of $6SiO_2$. The more familiar cases of isomerism were the nitrites and sulphites, and isomerism had also been ob-

served in the thiosulphates and the salts of the phosphorous acids. Attention was directed to some cobalt, platinum, and molybdenum compounds which showed this peculiarity. Another analogy between carbon and inorganic compounds was the curious and interesting catalytic action, referred to by Bredig under the title of "inorganic ferments." Colloid platinum solutions acted on many substances in the same way and under similar laws as enzymes. The whole subject was little known, but it suggested that the broader study of inorganic chemistry, especially in the light of our knowledge of the "organic" division of the science, was well worthy of much greater attention than it had received of late.

Dr. Russell, in moving the adoption of the Report, proposed a vote of thanks to the President, coupled with a request that he would allow his Address to be printed in the *Transactions*.

Prof. Thorpe seconded the motion, which was carried by acclamation.

After the President had returned thanks, the scrutators presented their report to the President, when he declared the following to have been duly elected as Officers and Council for the ensuing session :—

President—W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents who have filled the office of President—H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; James Dewar, M.A., LL.D., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; W. H. Perkin, Ph.D., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—Wyndham R. Dunstan, M.A., F.R.S.; P. F. Frankland, LL.D., F.R.S.; David Howard; Herbert McLeod, F.R.S.; Raphael Meldola, F.R.S.; H. A. Miers, D.Sc., F.R.S.

Secretaries—A. Scott, M.A., D.Sc., F.R.S.; W. P. Wynne, D.Sc., F.R.S.

Foreign Secretary—Sir W. Ramsay, K.C.B., LL.D., F.R.S.

Treasurer—Horace T. Brown, LL.D., F.R.S.

Other Members of Council—J. J. Dobbie, M.A., D Sc.; Augustus E. Dixon, M.D.; M. O. Forster, Ph.D., D.Sc.; A. Harden, D.Sc., Ph.D.; J. T. Hewitt, M.A., D.Sc.; C. A. Kuhn, Ph.D., B.Sc.; J. E. Marsh, M.A.; E. J Mills, D.Sc , LL D., F.R S.; S. U. Pickering, M.A., F.R.S.; S. Ruhemann, M.A., Ph.D.; J. A. Voelcker, Ph.D.; James Walker, D.Sc., F.R.S.

Anniversary Dinner.

The Anniversary Dinner of the Society took place at the Whitehall Rooms on Wednesday, March 25, at 7 p.m., when the Fellows and their guests dined together.

The President, in proposing the loyal toasts, said that when the Fellows of the Chemical Society last dined together they were mourning the loss of their great and venerable Queen, and were engaged in a sanguinary war. To-day they were in happier circumstances; the war cloud had disappeared, and that other cloud of suffering through which the King had to pass after his Accession was now but a memory. They might therefore now rejoice and join with new meaning in the old cry of "Long live the King."

Professor Thorpe, in proposing the toast of the Houses of Legislature, said that the theme offered many tempting possibilities. All would admit that both Houses showed an intelligent appreciation of the important part science plays in the conduct of human affairs nowadays, and in directing human development, even to the extent of preserving the national existence of the people for whom these Houses have to legislate.

Now, the House of Lords is singularly fortunate in that it possesses three at least of the most distinguished representatives, not only of British science, but of the science of the whole world—Lord Lister, Lord Rayleigh, and last, but not least, Lord Kelvin, whom we have the honour and pleasure of welcoming here to-night.

It was a circumstance unique in the history of any legislative assembly that there should be at one time three men of such world-wide prominence in the councils of any nation. In France such a thing does not happen; nor even in Germany, so often held up to us as an example of what should be in the relations of the State to science. The House of Commons is not so rich in scientific ornaments. It is true that she possesses in the person of the Secretary of the Royal Society, the Member for the University of London, a man who is a host in himself. As for Sir Herbert Maxwell, like Lord Kelvin, he is no stranger within our gates. His position as a literary man is well known to all. It does not seem to matter to him whether he is chronicling the achievements of some great master in the art of war or of some great master in the art of painting. On history, biography, fiction, natural history, his busy pen has left its mark. He is known in yet another sphere of action to several who are here to-night, and who have had the honour and pleasure of sitting under him on certain departmental committees in which, as a member of the Legislature, he has taken a leading part. Although all may not have seen the results of these inquiries from the same point of view, all are agreed in tendering Sir Herbert Maxwell their appreciation of his urbanity, courtesy, impartiality, and knowledge of procedure.

In responding for the House of Lords, Lord Kelvin pointed out the blood-relationship which exists between the peerage and modern chemistry, for was not the Hon. Robert Boyle "the father of modern chemistry and brother of the Earl of Cork?" But without straining this relationship too far, there was much in modern science which linked it to the peerage. We have the Marquis of Worcester with his steam-engine, Baron Napier and his logarithms, the Hon. Robert Boyle, Cavendish who added so enormously to our knowledge of electricity and chemistry, and who obtained argon as a bubble the size of a pin's head by burning the nitrogen of the air with oxygen, Lord Rayleigh, who has made litres and litres of argon, Lord Salisbury, Lord Blythswood, and Lord Lister. But it was not only because the House of Lords contained many scientific men, but because, as Professor Thorpe had remarked, it was a working and a useful part of the Legislature of the British Empire, that he had to thank them for the toast. As for himself, he would like to say that all his life he had tried to be a chemist. Physical chemistry and chemical physics make up the whole of science outside of biology, at the present day. A great deal has been heard of physical chemistry. With some modifications of its fundamentals, it had come to stay. We must now all be chemists, for chemistry is *the* science of the whole of matter. Gravitation has shown us great things at great distances. Cavendish pushed down the law of gravitation to small distances, but now we must go on down to infinitely smaller distances in connection with chemical affinity, which Cauchy supposed could act at distances infinitesimal with regard to the wave-length of light. The physicist must bow to the chemist to investigate these things. The largest part of physical science is chemistry, and the chemistry of the future is the whole of physical science.

Sir Herbert Maxwell, in replying for the House of Commons, said that in spite of all the kindliness infused into his allusions to the House of Commons, Professor Thorpe had given the impression that the atmosphere of the House of Lords was a purer and a loftier one. And so it is, but is that independent of the fact that so many of those who sit there have passed through the purgatory of the Lower House? Such are Lord Blythswood, Lord Avebury, better known as Sir John Lubbock, and many

others. When the connection between science and the Legislature was mentioned, he feared lest the proposer of the toast was going to contrast what was done in this country for science with what was done in other countries. At the present time, for example, he was chairman of a departmental committee to inquire into the administration of the meteorological grant, which amounts to £15,000. In the United States the grant for a similar purpose is a quarter of a million. Although all the members of the committee appointed by the Privy Council to inquire into the working and amendment of the Pharmacy Acts did not put the same construction on the evidence brought before them, each was ready to give to every other full credit for the faithful discharge of duty according to his lights. Had the report depended on himself alone, he would have felt serious misgivings, especially after many letters he had received from members of a very important profession, but he was much indebted to the Chemical Society for the aid rendered to him by its ex President, Professor Thorpe, its President-elect, Professor Tilden, and Dr. Stevenson. When it is considered how largely the use of poisonous substances has increased in agriculture, horticulture, and various other industries, he thought they were justified in coming to the conclusion that same relaxation of the restrictions imposed by the Pharmacy Act of 1868 had become urgent.

Sir W. T. Thiselton-Dyer said that it was with great pleasure that he proposed the toast of "Prosperity to the Chemical Society," especially as he had to couple with it the names of two great friends of his, those of the President, Professor Emerson Reynolds, and the Honorary Secretary, Professor Dunstan. To the former he owed much for introducing him many years ago to the society of the scientific men of the Irish capital, who were bound together by a *camaraderie* unknown in London. He understood that the President during the tenure of his office had travelled something like sixteen thousand miles in the performance of his duties. The Senior Secretary, whose scientific work he so highly appreciated, gives up his office after a decade spent in the service of the Society, and leaves work much more congenial to him to devote his energies to the task of co ordinating the Imperial Institute into something useful to the Empire, in which he would have the hearty co-operation of Kew. There must be something in the science of chemistry which for its own sake can call forth such enthusiasm and energy. When the Society meets a century hence, he could conceive that they would look back on the chemistry of the present time much as the transcendental mathematician looks on the arithmetic of the Board school. The chemistry of to-day is probably only the expression of a particular view of material structure —a mere calculus which may be dispensed with. The dream of his old teacher, Sir Benjamin Brodie, may yet be realised, and we may not only be able to say what compounds are possible, but be able to predict their properties, their structure, their form. But what is to be said with regard to life? Lord Kelvin long ago suggested that it came from the stars. After some work with which Professor Dewar had kindly associated his name, he had no hesitation in saying that he could see no difficulty in protoplasm passing through stellar space even though it could not be reduced to chemical laws.

The President said he rose with very mingled feelings to respond. He did not know that he could claim that chemists as a body were particularly modest, but he thought that he might justly claim that the Society which was represented here to-night did admirable work and did it well. There was no harm in proclaiming that the Society was prosperous; its Fellows numbered 2471, and its income has reached the respectable sum of £6200, which has enabled it to print a very large amount of work contributed by its Fellows, many of whom, in addition, it has been able to aid in a material way in the prosecution of their researches. They had always the certainty that truth acquired for its own sake would become of ultimate value to the human race. Now nothing contributes so much to the success of work in any department of human knowledge as a good working hypothesis. It is therefore interesting to note that they were in a measure celebrating the Centenary of the promulgation of the Atomic Theory. That great inspiration of Dalton's with regard to the discrete nature of matter seems to have been first made known in a tentative form to a select audience of nine persons. Now the whole world is the audience of the philosopher. It was invented to explain the chemical laws then known, and had exercised a most profound influence on the progress of science. It was the germ of that molecular theory of matter which pervades all chemistry and physics at the present time. Physicists seemed to expect them to think that all light and leading flows through them, and many considered that Dalton's theory has had its day, but he agreed with Lord Kelvin that it had a long day yet.

Professor Dunstan expressed the great gratification it had been to him to be officially connected for the last ten years with the Society, which continues to grow from year to year, and reflects not only the progress of English chemistry, but of the science of chemistry throughout the world. One circumstance he would always recall with the greatest pleasure, and that was the harmonious way in which the officers had always worked together in promoting the best interests of the Society. All acknowledge how much chemistry owes to Germany, and here to-night is to be seen, for the first time by the Society, the bust of Liebig, to whom, both as a discoverer and as a teacher, our science is indebted so much. This gift, which will soon adorn the rooms of the Society, they owed to the generosity of Dr. Messel.

The President-Elect, Professor Tilden, said that the pleasant duty of proposing the health of their guests had been assigned to him. Beside those whom they had had the pleasure of hearing, he might mention that they had with them the Director of the National Physical Laboratory, who was, also, most appropriately President of the Physical Society, the President of the Pharmaceutical Society, and the President of the Institute of Chemistry. He could assure the last named that although at one time it was feared that the Institute of Chemistry might interfere with the progress of the Chemical Society, he could assure its President that the Chemical Society looked with friendly eyes on its efforts to raise the qualifications of professional chemists, and to inculcate among its members those professional feelings with which every well-organised profession ought to be animated.

A secret which he had reserved for himself had been let out by Professor Dunstan. The bust of Liebig which they saw was said to be a faithful representation of the great master to whom the science of chemistry owed so much, and who was well known in England forty-five years ago. Has he come back, like the statue of the commander in *Don Juan*, to remind us of our misdoings? For in 1837 Liebig wrote that he had been staying for a long time in England and had not learned much. He thought that could an opinion be obtained from him now it would be very different, for since that time vast revolutions had taken place. In this country we are always a little late in starting, but when we do start we do our work thoroughly; and he thought that the activity, energy, enthusiasm, and quality of the work done by the Society was not surpassed by any other society on the face of the globe. He had been instructed to couple with this toast the names of Mr. Kempe, Treasurer of the Royal Society, and that of his old friend and pupil, Mr. Swinburne, President of the Institution of Electrical Engineers. He might say that with regard to the Royal Society the Chemical Society looks towards it much as a daughter looks towards her mother even after she has left the parental roof. The acquisition of the three magic letters F.R.S. is still the ambition of all the young

chemists of England, an ambition which has a very healthy influence as an incentive to the pursuit of scientific work. He hoped it would always be reserved as a prize for the successful worker, and awarded solely for additions to knowledge. Circumstances tempted him to ask them to join with this toast yet another well-known name, that of one of the Fellows of the Society, whose appearances are so rare that he comes almost with the prestige of a Foreign Member. All used to look upon Professor Lunge as an Englishman, but whatever he is now he trusted that he retained some kindly thoughts of bygone days spent in England.

There were two reasons Mr. KEMPE thought, why he had been asked to respond to this toast—one because he was the senior officer of the Royal Society present, and the other because he represented the law; but he was not on that account going to give them a speech of double length. To-night they had been brought together by the forces of chemical affinity, but soon the forces of dissociation must come into play; still, he ventured to hope that soon again the processes of synthesis would be re-established.

Mr. SWINBURNE said that it was very pleasant to have his old master, Professor Tilden, propose his name as one of their guests to-night. If, as a boy, he had ever any chemical microbes in him, it was by Professor Tilden that they had been fostered. Although all knew how unsafe it was to differ from Lord Kelvin on any point, he was going to claim chemical science as a small branch of that domain of science which he had the honour to represent, because the *Encyclopædia Britannica* says, and therefore it must be so, that all chemical action is but electrolysis. The foundations of chemistry have, on the whole, been more secure than those of most other sciences during these troublous times. Chemists did not suffer so much as electricians did, for they used to have one fluid, then two fluids, and now no fluid. They had to master a new theory almost every week or two. If there was one piece of advice he might be allowed to give, it would be to stick fast to their atoms and molecules.

Professor LUNGE said that he had been greeted by the President-elect as a guest, and in one sense he was so. He had the honour of being elected a Fellow of the Society thirty five years ago, but had never been able until that day to be present at a single meeting. When he was elected he resided in the far north, and his visits to London were few and far between, and now that he was in Zurich they were naturally still more rare, yet he never came to London without looking to see whether he could not attend a meeting of the Society. Now to-day he had been able to attend the Annual General Meeting, and had hoped to be formally admitted a Fellow. He found, however, that that was against the Bye-laws, for it was only at Ordinary Scientific Meetings that Fellows could be admitted. He was therefore just where he was before, and so far entitled to be considered as a guest. Since the freedom of Zurich had been conferred upon him he had become a citizen of Switzerland, but he always felt himself to be what Professor Tilden called him—an English chemist. Whatever he had done he owed to his twelve years of English training, so he owed a debt of gratitude to this country, and he was glad to have this opportunity of saying so and of thanking them for the kind way in which he had been received.

Iron and Steel Institute.—The Annual Meeting of the Institute will be held, by kind permission, at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 7th and 8th, 1903, commencing each day at 10.30 a.m. The Autumn Meeting will be held at Barrow-in-Furness during the first week in September. An influential reception committee has been formed, with His Grace the Duke of Devonshire, K.G., as Chairman.

NOTICES OF BOOKS.

Tests and Reagents, Chemical and Microscopical, known by their Authors' Names; together with an Index of Subjects. Compiled for the Use of Chemists, Microscopists, Pharmacists, Students, &c. By ALFRED I. COHN. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. Pp. iii.—383. 8vo.

THE author of this convenient manual is well known by his work "Indicators and Test Papers," which is already in its second edition. In preparing the present volume he has made use of the analogous pamphlets by Altschul, Schneider, and Wilder, as well as the material published in *Merck's Report* during the last three years.

The book is practically a dictionary of those tests known by their authors' names; it is alphabetical, with a subject-index of forty pages, forming an invaluable work of reference as it is, but would be of far greater value had Mr. Cohn thought it possible to append to each test a reference to the original paper in which it appeared, with the date. With the exception of occasional references to Fresenius and one to *The Analyst*, bibliographic data are entirely lacking. H.C.B.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

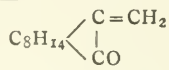
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 12, March 23, 1903.

Combination of Carbon Dioxide and Potassium Hydride.—Henri Moissan.—The author finds during a synthesis of the alkaline formates an example of the part which a very small quantity of water plays in a reaction. He proves experimentally that from $-85°$ to $+54°$ potassium hydride does not combine with absolutely pure gaseous carbon dioxide. During this interval of temperature the trace of water corresponding to the vapour tension of ice at $-85°$ is sufficient to start the reaction, owing to the heat which is evolved by the violent decomposition of a very small quantity of the alkaline hydride. After once starting enough heat is evolved to continue the reaction, and the change rapidly becomes total. During his experiments on the ordinary combination of carbon dioxide and the hydride, the influence of this trace of water is unimportant.

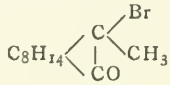
Catalytic Decomposition of Ethylic Alcohol by Finely Divided Metals; Regular Formation of Aldehyde.—Paul Sabatier and J. B. Senderens.—The authors find that the decomposition of ethylic alcohol into hydrogen and aldehyde is effected at a comparatively low temperature by means of copper. There is, in this case, no simultaneous formation of ethylene and no separation of water. The intervention of an oxide produced by reduction of water vapour is absolutely inadmissible, since there is no water vapour, and even if there were copper at 850° would be absolutely incapable of reducing it. The authors believe that the decomposition of the alcohol is caused by the production of an unstable metallic hydride which under certain conditions provokes the hydrogenation of the products. This action is supposed to be catalytic and will act in the case of many primary and secondary alcohols.

Barium Sub-salts.—M. Guntz.—The author investigates the action of sodium on the halogen compounds of barium and prepares the sub-salts BaI NaI, BaBrNaBr, BaClNaCl, BaFNaF, salts which have never been obtained before. If these salts are heated in vacuo to about 700°, the sodium volatilises, leaving the ordinary halogen compound, for example, $BaClNaCl = BaCl_2 + Na$.

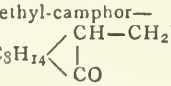
Methylmonobromo-camphor, Bromomethyl camphor, and Methylene-camphor.—J. Minguin.—By a modification of M. Haller's method the author prepares methylene-camphor—



and from this the bromine derivative—



and again, bromomethyl-camphor—



Hydration of Acetylenic Acids. New Method of Synthesis of the Acids and the Non-substituted β-Ketonic Ethers.—Ch. Moureu and R. Delange.—A classic method of synthesising acetones corresponding to the general formula $R-CO-CH_2-R'$ consists in fixing the elements of water on to the acetylenic hydrocarbons, $R-C\equiv C-R'$. The authors apply this reaction to acids possessing an acetylenic function in addition to the carboxyl ($R-C\equiv C-CO_2H$) in order to convert these into ketonic acids, $R-CO-CH_2-CO_2H$ or $R-CH_2-CO-CO_2H$. Such a reaction takes place in a perfectly satisfactory manner by the action of caustic alkalis. The oxygen of the water fixes itself on to the acetylenic acids in the β position with regard to the carboxyl. Such a reaction gives, therefore, a new method of synthesising the non-substituted β ketonic acids, $R-CO-CH_2-CO_2H$.

Action of Phosphorus Trichloride on Glycol.—P. Carré.—The action of phosphorus trichloride on glycol causes the formation of 70 to 75 per cent of the product $P_2(OCH_2)_4Cl_2$. The trichloride or the evolved hydrochloric acid act also as a chlorinater, forming glycol chlorohydrine, which itself takes part in the reaction, giving the compounds $PCl_2OCH_2-CH_2Cl$ and $P.Cl.OH.OCH_2CH_2Cl$; this latter compound being insoluble in anhydrous ether, the other two being soluble. At the same time a small quantity of phosphorous acid is formed. These products are decomposed by water, hydrochloric acid being liberated. The first gives a phosphorous ether, $P_2(OCH_2)_4(OH)_2$, which is very unstable, easily losing 1 mol. of glycol when acted upon by water, and giving the ether $P_2(OCH_2)_2(OH)_4$. These two ethers behave as di-acids towards helianthine and phthalein. The latter gives phosphorus ether and glycol chlorohydrine, acting towards helianthine and phthalein as a mono-acid. These compounds are both slowly saponified by cold water, and rapidly by boiling water.

Action of mixed Organo-magnesium Compounds on Amine Compounds.—Louis Meunier.—The mixed organo-magnesium compounds described by Grignard react on ammonia, and the primary and secondary amine groups, borrowing an atom of hydrogen to form the carbide corresponding to the organo-magnesium compound, and substituting in its place the monovalent radical, MgX (X being a halogen element).

Pyrogallol-sulphonic Acids.—Marcel Delage.—In a previous paper the author described the two pyrogallol-sulphonic acids and their principal salts, especially those of barium and calcium. He now describes the preparation and properties of the strontium salts of the same two acids.

MISCELLANEOUS.

Royal Institution.—On Tuesday next (April 21st), at 5 o'clock, Prof. Allan Macfadyen will deliver the first of three lectures at the Royal Institution on "The Blood and some of its Problems"; on Thursday (April 23rd), at the same hour, Prof. Dewar commences a course of three lectures on "Hydrogen—Gaseous, Liquid, and Solid"; and on Saturday (April 25th), at 3 o'clock, Prof. Langton Douglas begins a course of two lectures on "The Early Art of Siena." The Friday Evening Meetings will be resumed on April 24th, when the Hon. R. J. Strutt delivers a discourse on "Some Recent Investigations in Electrical Conduction"; on May 1st the discourse will be delivered by Prof. W. J. Pope on "Recent Advances in Stereochemistry"; and on May 8th, by Mr. Rider Haggard on "Rural England."

MEETINGS FOR THE WEEK.

TUESDAY, 21st.—Royal Institution, 5. "The Blood and some of its Problems," by Prof. Allan Macfadyen, M.D., &c.

WEDNESDAY, 22nd.—Society of Arts, 8. "Modern Bee-Keeping," by Walter Francis Reid, F.C.S.

—— Chemical, 5.30. "The Velocity and Mechanism of the Reaction between Potassium Ferricyanide and Potassium Iodide in Neutral Aqueous Solution," by F. G. Donnan and R. le Rossignol. "A Microscopic Method of Determining Molecular Weights," by G. Barger. "Note on the Spectrum of Pilocarpine Nitrate," by W. N. Hartley. "Isomeric Change of Dipropionanilide into Propionyl-*p*-aminopropiophenone," by F. D. Chattaway. "Note on the Formation of the Di- and Hexamethylammoniacal Chlorides of Cadmium," by W. R. Lang.

THURSDAY, 23rd.—Royal Institution, 5. "Hydrogen—Gaseous, Liquid, and Solid," by Prof. Dewar, F.R.S., &c.

—— Society of Arts, 4.30. "The Province of Sind," by Herbert Mills Birdwood, C.S.I., M.A.

FRIDAY, 24th.—Royal Institution, 9. "Some Recent Investigations on Electrical Conduction," by the Hon. R. J. Strutt, M.A.

—— Physical, 5. Exhibition of Elementary Apparatus, by Mr. Croft. "An Electrical Thermostat," by H. Darwin. "Dimensional Analysis of Physical Quantities and the Correlation of Units," by A. F. Ravenshear. "Note on the Dimensions of Physical Quantities," by R. J. Sowter.

SATURDAY, 25th.—Royal Institution, 3. "The Early Art of Siena," by Prof. Langton Douglas, M.A.

ERRATUM.—P. 162, col. 2, line 21 from bottom, *for* "three" *read* "two."

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THE CHEMICAL NEWS

VOL. LXXXVII., No. 2265.

APPLICATION OF THE THEORY OF ELECTRIC BATTERIES TO THE QUANTITATIVE SEPARATION OF METALS.

By A. HOLLARD.

WHEN we plunge a strip of any metal into the saline solution of a more electro-negative metal, the latter is deposited on the former. This constitutes an analytical process and separation well known but rarely applied in quantitative analysis.

As a matter of fact, the deposits obtained are generally spongy, very oxidisable, and difficult to wash. Sometimes, however, the deposit is adherent, but in that case it rapidly and completely emprisons the precipitating metal, and as this latter can no longer go into solution the precipitation is arrested.

We can prevent these drawbacks and make the method quantitative in the following manner:—Suppose that, in a solution containing both nickel and zinc, we wish to precipitate the nickel only, by means of a strip of zinc. We take a vessel divided into two compartments by a membrane of vegetable parchment (sulphurised paper). Into one of these compartments we pour the solution containing both the nickel and zinc (B), and in the other one a saline solution (A), which only needs to be a conductor of electricity, such as a solution of sulphate of magnesium, for example. The strip of zinc for precipitating the nickel must be plunged, not in the solution containing the nickel, but in the solution of sulphate of magnesium. A strip of platinum is placed in solution B, and we connect the platinum to the zinc by means of a copper wire. In this manner we have constructed a double fluid, reversible battery of the Daniell type, in which the current flows from the platinum to the zinc by the copper wire, and from the zinc to the platinum through the solutions. Thus we should produce an electrolysis of the nickel salt, with the deposition of pure nickel on the strip of platinum.

In practice we proceed in the following manner:—The nickel and the zinc, which are both brought to the form of sulphates in solution, are contained in a beaker of 650 c.c. capacity, and 7 c.m. diameter The solution should contain an excess of 20 c.c. of ammonia at 22° B., and 100 grms. of dry sulphate of ammonia, and should occupy about 250 c.c. A cylinder of platinum gauze, 65 m.m. long, 43 m.m., and 35 m.m. diameter at the two ends, is placed in the beaker. A cylinder of glass 55 m.m. diameter, closed at one end by a parchment paper diaphragm, is also placed in the solution so that the diaphragm is as near to the platinum gauze as possible without touching it. This tube forms the internal compartment of the apparatus. A solution of sulphate of magnesium at 250 grms. per litre is poured into this tube until it is 70 m.m. deep. Sulphate of magnesium is chosen in this case, because it is one of the salts that has no chemical action on zinc. Finally, a disk of amalgamated zinc is plunged into this latter solution; it is 5 c.m. diameter, and is held by a copper wire insulated along its length by an indiarubber tube, and connected at the end to the end of the platinum electrode.

The zinc disc is arranged about 15 or 20 m.m. above the parchment, and is pierced with several holes to allow the free circulation of the liquid in the internal compartment. The outer liquid must be kept up to 95° during the operation. After a few hours the nickel is deposited completely on the electrode in a very adherent metallic layer. The electrode is then withdrawn and washed thoroughly, and left for ten minutes in distilled water; it is then dried and weighed.

It may be asked, what are the advantages of this method of separation over the methods given in electrolytic analysis? Electrolytic analysis, in principle, is based on the fact that each metal is deposited at a definite tension of its own—so definitely so, that by gradually increasing the tension of a current passed through an electrolytic cell containing a mixture of metals, the deposition of each one ought to be effected in turn.

In reality, there are cases where the tensions of polarisation of the metals are too close to each other to permit the separation of one of them without the others being carried with it. This is precisely the case with nickel and zinc, which we have never succeeded in separating completely, no matter how feeble the currents used; for example, in ammoniacal sulphate solution the nickel always carries zinc with it; in cyanide of potassium solution, where the order of the tensions is inverted, because of the complex nature of the salts, the zinc always carries nickel with it.

On the other hand, the present method enables us to separate two metals of which the tensions are very close to each other; it is sufficient to make the negative pole with a disc of the metal having the highest tension, and the other metal will be precipitated alone.*

Experimental Results.

	Amount taken. Ni. Grm.	Amount taken. Zn. Grm.	Ni deposited. Grm.
1	0·2000	1·0	0·2026
2	0·2000	0·5	0·1995
3	0·2500	1·0	0·2499
4	0·2500	1·0	0·2525
5	0·5000	0·0	0·4989
6	0·4500	1·0	0·4506
7	0·5000	1·0	0·5048 (contained a little zinc)
8	0·0500	1·0	0·0524

The amounts of nickel and zinc were not weighed, but were measured with pipettes from titrated solutions.

We see from the above table that the method is applicable to any proportions of nickel and zinc; still, the mixture should not contain more than 1 grm. of zinc nor more than 0·45 grm. of nickel, or there is a liability to deposit zinc at the same time as the nickel.

Experiment No. 7 showed that with 0·5 grm. of nickel and 1 grm. of zinc there was zinc carried down with the nickel. When there is no zinc present in the solution, we can deposit at least 0·5 grm. of nickel in the pure state. (See experiment 5).

These limitations of the quantities of nickel and zinc find their explanation in the theory I am about to put forward.

The theory of this present method of separation is no other than that of reversible batteries. The tension of the solution P of the precipitating metal, in this case zinc,† being greater than the tension of solution P′ of the precipitated metal; in this case, the nickel,‡ there is a positive electric tension established between the two metals which can be determined by Nernst's formula:—

$$e = \frac{K}{v} \log \frac{P}{C} - \frac{K}{v'} \log \frac{P'}{C'},$$

* The order of the tensions of the principal metals is as follows, commencing with the highest:—Zn, Cd, Fe, Co, Ni, Sn, Pb, H, Cu, As, Bi, Sb, Hg, Ag, Pd, Pt, Au. This order is the same as that of the electric tensions.

† The idea of *tension of solution* has been suggested in the theory of ions by the analogy that has been established between the tendency the body has to pass to the state of ions and the tendency it also has to pass to the state of vapour. In the same manner that the second has been named vapour-tension, the measurement of the former is called tension of solution.

‡ The order of the tensions of solution is the same as that of the tensions of polarisation given in a previous footnote.

K is a constant for a constant temperature; v and v' are the valences of the precipitating and the precipitated metals, C and C' the concentrations of these two metals.

In the formula we have put C and C', the concentration of the metals, instead of their osmotic pressures p and p', which ought to be inserted, because, C and C' are proportional to p and p', on account of the relatively great dilution of the solutions with which we are dealing.

We see, according to this formula, that when the concentration C of the zinc, in the interior compartment, increases on account of the deposit of nickel on the platinum electrode, e will diminish. Therefore, there should not be too much nickel to be deposited; still we can easily deposit 0·45 grm. According to the same formula, we see see that if the concentration of the nickel diminishes, e tends towards zero, which means that the nickel cannot be deposited entirely.

This is what happens if we take neutral sulphate of nickel, but we have to deal with a solution which contains a large excess of sulphate of ammonia and ammonia; that is to say, a solution containing a large concentration of $\overset{+}{H}$ ions; from this it follows that C' does not represent the concentration of the nickel ions, but a mean between the concentration of the ions $\overset{++}{Ni}$ and $\overset{+}{H}$. This hydrogen is being given off throughout the duration of the electrolysis.

Thus, if we wish to generalise the method for other separations than that of nickel and zinc, care must be taken to have an excess of ammonia or acid, or of some other body capable of forming the ions $\overset{+}{H}$.

In reality, the phenomenon is complicated by the secondary actions, which must always be remembered if we wish to extend the method to other separations than that of nickel and zinc.

1. The concentration of the sulphate of zinc which accompanies the nickel in the solution, must not be too great, for in that case this salt on the one hand, and, on the other, the dilute solution of sulphate of zinc that is formed in the other compartment by the dissolving of the disc of zinc, might constitute a *battery of concentration* (Zn, dilute $ZnSO_4$, Pt, concentrated $ZnSO_4$, Zn and Pt being the poles of the battery; that is to say, the disc of zinc with its wire, and the platinum electrode) sufficiently strong to raise the total electric tension of the system to a point at which the zinc might be precipitated with the nickel; this is what we have observed when the solution of nickel contained 2 grms. of zinc and over. For this reason we recommended above not to have more than 1 grm. of zinc in the solution of nickel.

2. The sulphate of zinc formed in the solution of sulphate of magnesium by the solution of the zinc, attacks the zinc disc, especially when heated; there we get a voltaic couple which produces another increase of electric tension, an increase which we have kept as low as possible by arranging to have the compartment containing the zinc disc in the coolest part of the apparatus. The concentration of this sulphate of zinc increases gradually as the nickel is deposited, and this augmentation increases the attack on the zinc disc, and consequently the tension of the voltaic couple, which eventually causes the precipitation of the zinc with the nickel. Fortunately this increase of concentration at the same time causes the tension of the battery of concentration to decrease, as well as the tension of the principal battery (see Nernst's formula above), so that we can deposit up to 0·45 grm. of pure nickel, even when the solution of nickel is accompanied by 1 grm. of zinc. When the nickel is alone, we can get a much greater deposit, for in this case there is no battery of concentration. From what has preceded it results that the amount of nickel deposited in the pure state may be the greater in proportion as the nickel is accompanied by less zinc (for then the effect of the battery of concentration is reduced in like proportion), and inversely, that the amount of zinc that accompanies the nickel may be all the greater as the nickel is less (for then the effect of the voltaic battery is reduced in like amount). By never exceeding 0·45 grm. of nickel and 1 grm. of zinc in the solution, we can be always certain of obtaining pure nickel.

3. Finally, there is another secondary phenomenon which is not produced by sulphate of zinc, but which may occur with a certain number of salts, so it is as well to examine it in order that our discussion of this method may be complete. We mean the transportation of these salts, during electrolysis from the cathode (here the platinum) to the anode (here the precipitating metal). This is called Hittorf's phenomenon. It is necessary, therefore, to see with regard to each metal whether it forms a salt not submitting to Hittorf's phenomenon, and if it is preferable to work at any one temperature rather than another, for the loss of concentration round the cathode (and round the anode) varies with the temperature. Thus the method cannot be applied to the whole category of salts. There can be no question especially of applying it to sulphate of copper, the ions $\overset{++}{Cu}$ passing from the anode very rapidly.—*Bull. Soc. Chim.*, Series 3, vol., xxix., No. 3.

A METHOD OF FREEING COMMERCIAL METHYLATED SPIRIT FROM MINERAL OIL.

By A. P. IBBOTT.

Commercial methylated spirit contains, in addition to aldehydes and other removable substances, a certain amount of mineral oil. Apart from these impurities, methylated spirit might be used by the chemist for the large majority of his operations in place of the costly ethyl alcohol. Where ethyl alcohol reacts with other substances to form a desired product none but the pure ethyl alcohol must be used, but in the large number of cases where it is employed as a solvent, and for crystallisations, the presence of a small quantity of methyl alcohol is usually harmless, and pure methylated spirit might be used at a fraction of the cost of absolute alcohol.

Pure methylated spirit is, however, impossible to obtain unless under conditions which are impracticable except to those who employ it on a very large scale. A method is well known for removing the aldehydes, &c., which consists in distilling the spirit with caustic potash, followed by treatment with an oxidising agent, such as potassium permanganate or bichromate.

The mineral oil remains, however, after this treatment, and if such partially purified spirit is diluted with water the oil is thrown out of solution, and appears in suspension, rendering the liquid quite opaque. The presence of this oil unfits it for all the ordinary purposes of the chemist. The oil will not, in any reasonable time, separate in a layer so as to allow of the spirit being drawn off by means of a separator, and filtering is useless, as the particles of oil pass through the closest-grained filter-paper.

If, however, the mixture of spirit and water is saturated with common salt, and then filtered, the resulting filtrate is found to be perfectly clear. Methylated spirit may therefore be freed from mineral oils by this method, the cost of which is infinitesimal.

The methylated spirit, after treatment with caustic potash, &c., as above, is diluted with two and a-half times its bulk of water, enough salt is added to *thoroughly saturate* the mixture, which is then shaken vigorously for five minutes. After standing half-an-hour, the mixture is filtered through a paper well wetted with water. The filtrate is clear, and consists of a mixture of brine and spirit, from which a 90 per cent alcohol can be obtained in two fractional distillations. This can of course be further freed from water by the usual methods.

If the distillate should still give a slight milkiness on the

addition of water, it is an indication that sufficient water was not added in the first operation to throw the whole of the oil out of solution, but the quantity stated (two and a-half volumes) is usually sufficient.

From the writer's experiments, it would appear that the salt causes the oil to separate as a layer on top of the mixture of brine and spirit, but the quantity of oil is so small that the layer cannot be distinctly observed. Or possibly the salt causes the particles of oil to cohere into larger particles which will not pass through the filter-paper. In any case, filtration has been found to yield better results than are obtained by using a separator.

ON THE

DETERMINATION OF MOISTURE IN HONEY.*

By FRANK T. SHUTT, M.A., F.I.C., F.C.S.,
and
A. T. CHARRON, M.A.

The investigation which gave rise to the work recorded in this paper was undertaken to ascertain what difference in composition—if any—existed between honey extracted from capped and uncapped comb. Apiarists term the latter immature or unripe honey, and contend that it is of a thin and inferior quality, and, therefore, when placed upon the market, apt to injure the sale of mature or ripe honey taken from fully capped comb. Further, it is held that "unripe" honey materially affects the latter's keeping quality.

Among the first determinations attempted was that of the water-content of the honeys, and the difficulties that were at once met with in obtaining results of a concordant and reliable character led us to examine the various methods now in vogue for estimating moisture in such saccharine substances.

Drying on Asbestos in Glass Tubes at approximately 98° C. in Steam bath.

In all essential features, this method is that recommended by Macfarlane for estimating moisture in milk, butter, and many other articles of food that are already fluid or can be readily brought into this condition. The honey was weighed in a weighing bottle and then washed out into a 100 c.c. graduated flask and made up to the containing mark. An aliquot part of the solution was run into each tube containing a sufficiency of asbestos to act as an absorbent. The tubes were then dried in racks in a steam-oven at atmospheric pressure and maintained at a temperature of (approximately) 98° C. We presume that this is essentially the method and *modus operandi* followed in obtaining the greater number of the results recorded in the *Bulletin* (No. 47) on honey, issued by the Inland Revenue Department, Canada.

Unfortunately, this convenient method proved exceedingly unsatisfactory, it being found impossible to obtain constant results. The longer the period of drying, the greater the loss. Even after five days' drying, the tubes continued to lose in weight—due, undoubtedly, to the continued decomposition (dehydration) of the levulose, which constitutes practically 50 per cent of the saccharine matter of honey.

In the following table we have arranged the moisture-content of twelve samples of honey as determined at the expiration of forty-eight hours, seventy-two hours, and ninety-six hours. In the first series, each tube received 20 c.c. of an approximately 20 per cent solution; and in the second series, 10 c.c. of an approximately 5 per cent solution. The percentages of moisture, as calculated from the specific gravity determination, are also given.

* From the *Transactions of the Royal Society of Canada*, vol. viii, p. 35.

(In all the estimations of moisture and solids, as calculated from the specific gravity of the diluted honey—taken at 15·5° C.—the following formula has been employed:—

$$W = \frac{D - 1000}{3\cdot85 \times M}.$$

W = Per cent of solids in honey.
D = Density of diluted solution of honey.
3·85 = Increase of density for each 1 grm. of sugar or other carbohydrate in 100 c.c. of the liquid.
M = Grms. of honey in 100 c.c. of diluted solution).

TABLE I.—*Moisture in Honey, as Determined in Steam-bath at 98° C.*

No.	From 20 per cent (approximately) solution.			From 5 per cent (approximately) solution.		Calculated from sp. gr. of diluted honey.
	48 hours.	72 hours.	96 hours.	48 hours.	72 hours.	
	Honey from Fully Capped Comb.					
1.	21·91	22·82	24·17	23·40	25·40	17·93
	20·30	22·19	22·98	25·68	26·48	
2.	21·86	22·38	23·38	25·80	26·20	17·88
	21·17	21·89	23·13	26·28	26·50	
3.	21·56	23·29	24·01	29·40	30·80	18·76
	20·56	21·44	22·76	28·24	29·72	
4.	24·43	24·48	26·27	28·94	30·70	19·55
	23·00	23·70	25·53	29·10	31·10	
	Honey from Partially Capped Comb.					
5.	25·05	26·91	27·73	29·78	31·54	19·49
	24·78	25·78	26 93	31 16	32·28	
6.	27·29	27·86	29·37	32·08	33·80	22·29
	27·56	28·50	29·49	32 18	33·30	
7.	28·41	29·57	30·86	33·80	35·88	23·27
	27·59	28·50	29 59	32 08	34·36	
8.	25·65	27·59	27·66	32·10	33·90	23·92
	26·14	27·63	28·14	33·00	35·72	
	Honey from Uncapped Comb.					
9.	23 68	24·86	25·47	30·40	31·76	19·57
	23·96	24·63	25·32	28·56	30 04	
10.	22 82	24·10	24·88	28·54	29·34	18·25
	23·07	23·98	24 97	28·48	30·36	
11.	23·34	24·65	25·73	27·58	29·76	19·24
	22·87	24·19	25 91	28·76	29·60	
12.	25·59	27·06	27·68	32·26	32·86	22·69
	26·65	28·10	28·58	32 90	34·22	

A detailed consideration of the data is unnecessary, but the more important deductions from them may be briefly stated as follows:—

1. That, assuming the results from the specific gravity determination to be approximately correct, a drying period of forty-eight hours at 98° C. gives too high a percentage of moisture, the excess being about 5 per cent.

2. That the longer the drying period, the greater the loss; that is, the decomposition of the levulose is continuous, This fact, that it is practically impossible to dry to a constant weight, is in itself sufficient to condemn the method.

3. That higher percentages of water are obtained from the 5 per cent than from the 20 per cent solutions of honey, showing that there is a more rapid decomposition of the levulose when using the more dilute solution.

Drying on Asbestos in Glass Tubes at 70° C. to 75° C. in Steam-bath.

Our next step was to ascertain the moisture-content, drying between 70° C. and 75° C.—the other conditions being the same as in the first series. Each tube contained 10 c.c. of an approximately 12 per cent solution of honey. The samples, though corresponding with those of the first series, were not identical with them.

TABLE II.—*Moisture in Honey, as Determined in Steam-bath at 70° C. to 75° C. Solution, approximately 12 per Cent.*

No.	20 hours.	27 hours.	31 hours.	36 hours.	Calculated from sp. gr. of diluted honey.
	Honey from Fully Capped Comb.				
1.	19·36	19·82	20 03	20·07	15·46
	19·95	20·29	20·50	20·90	
2.	19·52	19·87	19·99	20·co	16·95
	18·78	18·88	19·24	19·42	
3.	20·63	20·52	21·29	21·51	15·89
	19·59	20·16	20 67	20·44	
4.	20·20	20·59	21·12	20·91	15·84
	20·07	20·66	20·75	21·07	
	Honey from Partially Capped Comb.				
5.	23·00	23·49	23·87	23·71	19·12
	22·13	22·39	22·67	23·12	
6.	24·89	25·19	25·44	25·46	20·63
	25·41	25·87	26·21	25·91	
7.	25·23	25·46	25·85	26·19	20·68
	24 96	25·26	25·91	26·18	
8.	23·45	23·88	24·59	24·73	21·03
	24·00	24·06	24·78	25·33	
	Honey from Uncapped Comb.				
9.	21·20	21·77	21·69	22·c9	17·83
	21·46	21·56	21·81	21·62	
10.	21·26	21·73	21·61	22·00	16·59
	20·69	20·93	21·09	21·00	
11.	21·52	21·79	22·05	22·14	39·42*
	21·70	22·21	22·34	22·09	
12.	20·24	21·11	21·30	20·86	41·20*
	20·40	21·01	21·18	21·22	

* Found to be slightly fermented.

From these data we note that drying, even at this lower temperature (70—75° C.), for a period of twenty hours, gives results much higher than those obtained from the specific gravity estimations; and, further, the percentages of moisture—or rather, of loss—increase with continued heating, though not so rapidly as when a temperature of 98° C. is used (see Table I.).

(To be continued).

ON A METHOD OF DEMONSTRATING NEWTON'S COLOURS BY TRANSMITTED LIGHT.

By H. N. DAVIS.

IT is well known that if white light be passed through a thin film, part of it will be reflected twice within the film and will cause interference and colour phenomena. These are usually very faint because the amount of light that is thus reflected is so small as compared with what passes directly through as to have but a slight effect. If, however, the same wave-front be passed through a uniform series of films, successive portions of certain colours should be blotted out in each film, while other colours which get through the first film without interference, should emerge from each of the other (similar) films without interference, and the colour effect should be cumulative.

At the suggestion of Professor Barus, these surmises have been empirically verified, and excellent results obtained. If a number of wire rings of the same size be mounted in parallel planes, and dipped together into a soap solution, their planes being kept perpendicular to its surface, a suitable series of films results, through which light can be passed and caught on a sheet of paper, showing the desired phenomena very beautifully. Since each film, under the action of gravity, is a very thin wedge, the colours are in horizontal bands, appearing first at the top (where the wedge is thinnest) and moving slowly down across the field as the films evaporate, to be succeeded by other bands of lower orders. Indeed good films will often hold until two-thirds of the field is coloured with the yellowish-brown of the first order. And if the paper be replaced by a good lens, and the colours projected on a large scale upon a suitable screen, they can be strikingly demonstrated to a class. Some of the effects obtained in this way are most magnificent, even rivalling the best of our autumn sunsets, until it is only with reluctance that one concedes the essential dissimilarity between the two phenomena. In practice, the important thing seems to be uniformity in size and alignment in the set of rings. I have found it convenient to make them some 5·5 c.m. in diameter, using galvanised iron wire ($d = 1·2$ m.m.) and forming each around a pattern of wood or metal, the ends being twisted together into a sort of handle. Such rings can be temporarily strung on three rods, notched at appropriate intervals to insure parallelism in the planes of the rings, while the "handles" are being clamped between two pieces of soft wood. The rings should be at least a centimetre apart to avoid cylindrical and irregular films, and from fifteen to thirty are sufficient. A tin trough of such dimensions as just to admit the set facilitates the dipping.

During the course of this experiment, before the films have become thin enough to show colours, certain other phenomena of a circulatory character are very noticeable. These may be studied most easily in the projected image of a single film, and for observations on conditions immediately after formation, it is convenient to support a ring on the shorter branch of a J-shaped "handle" and to fix it permanently in the focus of the projecting lens, a narrow trough being raised so as to submerge the ring when necessary. The moving images are of two kinds, one corresponding to pear-shaped air-bubbles running up at the sides of the film, the other to spheroidal drops running down through the middle. These sets of images are always of opposite colours, and if, under given circumstances, the air-bubbles show white and the drops black, then moving the film some 4 c.m. away from the lens will reverse the colours, the bubbles showing dark and the drops white. From this it is evident that the latter act as convex lenses with real foci (bright spots) some 2 c.m. in front of the film, while the bubbles are concave lenses with virtual foci 2 c.m. behind it.

These air-bubbles require but little explanation, but the drops are more interesting. The happenings in a typical film (dipped at a time $t = 0$) are as follows: At first its image is clear, but almost immediately a few large drops appear at various parts of the film and begin to descend. These "wanderers" are much larger than their successors ($d = 0·5$ or $0·6$ m.m.) and their number varies from one to a dozen, being largest when a preceding film has dried on the ring and has not been removed. At $t = 1$ sec. a "skirmish-line" has formed about a third of the way down, above which line the film is closely dotted with drops. This travels down in the film about as fast as do the colour-bands later, reaching the bottom at $t =$ about 8 sec. The drops in its front rank are usually small, but a half a centimetre behind come the largest of the "ordinaries" ($d = 0·2$ to $0·3$ m.m.) and after these a succession of smaller ones until (at $t = 60$ to 100 sec.) the film begins to show colours and great viscosity is noticeable. The size of the average drop is some 0·2 m.m. and, roughly speaking, the size of those passing a given point decreases as t increases. The velocity of descent varies from 0 to 7 m.m. per sec (that of the wave front averaging 5·7 m.m. per sec.) and is greater (1) for large drops, (2) for drops near the bottom of the ring, and (3) at times corresponding to small values of t, but, if other things are equal, is nearly the same at all points in the

same horizontal line. A number of observations gave an empiric formula $v^2 = 2p(y-q)$ (y being the distance from the top of the ring, and p and q functions of t, the former decreasing—very rapidly at first—and the latter increasing as t increases). This formula is, of course, a rough approximation, but analogies between it and $v^2 = 2gs$ are very interesting. These "drops" are not simply bulges due to variations in the surface tension of a film (for similar phenomena appear in the image of a thin glass cell filled with solution), but are little globules floating in the liquid, composed of a more concentrated solution with greater density and refracting power, and with a surface tension with respect not only to air but to the rest of the solution; though the process by which such definitely separated globules are formed is not quite clear.

It is not unlikely that further study of the nature, form, and velocity of such descending masses, both in films and in thin cells (where they are spheres and the surrounding medium is stationary) may lead to a method of investigation not only of changes in viscosity due to evaporation, but possibly also of the problems of surface-viscosity, in connection with which further knowledge would be very desirable.—*American Journal of Science*, [4], xv., No. 87.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending March 31st, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Charles Perrin, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, April 11th, 1903.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 211 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 211 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month of March was 3·03 inches; the average fall for March is 1·47 inches, thus showing an excess of 1·56 inches; and the previous deficit of 0·51 inch is converted into an excess of 1·05 inches for the first three months of the year; the excess equals 19·6 per cent on the thirty-five years' average.

The conditions prevalent during the first quarter of the year are the first sign of a return to the normal rainfall in the Thames Valley during the last eight years; the conditions since the year 1895 having been quite exceptional.

The organic matter in solution, chiefly of vegetable origin, during the past month has exceeded the mean average amount of the last ten years. The excess is 20 per cent above the average. This would appear a considerable amount, unless regard is had to the fact that the total absolute amount present, even under the most disadvantageous climatic conditions, is always a small quantity. The present condition, however, is not exceptional, because substantially the same amount of organic matter was present in the Thames-derived waters during the winter months of 1898-9 and 1899-1900.

Unless with a much-increased staff and expenditure, it would be impossible to examine a larger number of samples than the 700 or 800 a month which, up to the present, we have regarded as sufficient to check the daily working of the various Water Companies. During the whole period of our conduct of the chemistry and bacteriology of the London Water Supply, now extending over twenty-three years, we have always acted as a perfectly independent authority, and no interest has been in our case more paramount than that of the water consumers. Our duty has been to endeavour to make the Water Companies work up to the highest efficiency, and we can say with perfect confidence that the general condition of the supply was never more carefully superintended and more satisfactory. The long series of more than 50,000 chemical and 35,000 bacteriological analyses that have been permanently recorded will always be a guide of the greatest importance in governing the operations of purifying the supplies from the Thames and Lea.

Our bacteriological examinations of 360 samples taken during the last month have given the results recorded in the following table. Besides these samples we have examined 225 others from special wells, standpipes, &c., making a total of 585 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	335
New River, filtered (mean of 78 samples) ..	11
Thames, unfiltered (mean of 26 samples) ..	9337
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 180 samples)	27
Ditto ditto .. .. highest	212
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 25 samples) ..	582
River Lea, from the East London Company's clear-water wells (mean of 25 samples) ..	29

Of the 283 daily samples taken from the filter-wells of the Metropolitan Water Companies, five samples, or 1·7 per cent, were sterile; fifteen samples, or 5·3 per cent, contained more than 100 microbes per c.c.; and five of these contained more than 150. The mean number of microbes in the samples containing more than 100 per c.c. was 136, against a corresponding mean of 144 in the 3·2 per cent excess samples of the month of February.

Practically the water has maintained the same bacteriological condition as it had last month.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

Optical Properties of the Oximidocyanacetic Ethers.—P. Th. Muller.—The optical examination of these bodies leads to one or the other following alternatives:—1. Either the nitroso-cyanised derivatives do not possess the constitution attributed to them; that is to say, they do not contain, at the same time, the radicals CN and NOH or NOR. It appears, however, from their synthesis from nitrous acid and the cyanacetic ethers that we cannot give them any other formula than NC—C—COOR and NC—C—COOR (with NOH and NOR respectively). 2. On the other hand, and this is the conclusion we have adopted, the two negative nitro-radicals CN and NO, have a mutual influence in raising their refractive power as well as their dispersive power. The double bond between the carbon and the nitrogen possibly plays a definite part, as has been observed before in other cases.—*Bull. Soc. Chim.*, Series 3, xxviii., Nos. 20—21.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, April 2nd, 1903.

Prof. W. A. TILDEN, D.Sc., F.R.S., President, in the Chair.

MESSRS. T. E. Wallis, R. C. Farmer, and H. W. Bywaters were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Godsell Burghard, 180, High Holborn, W.C.; Edwin Jesse Fairhall, 29, Winsham Grove, S.W.; Norbert Van Laer, 69, Calais Road, Burton-on-Trent; Henry Wolff Levy, Chancery Lane, Melbourne; Alfred Ernest Moore, B.A., B.Sc., St. John's College, Battersea, S.W.; George M. Norman, B.Sc., 5, Watford Villas, Battersea Park, S.W.; George Harry Parry, The Level, Brierley Hill, Staffordshire; James C. Smith, B.Sc., 57, Great Ormond Street, W.C.

Of the following papers, those marked * were read:—

*51. "*The Dioximes of Camphorquinone, and other Derivatives of Isonitrosocamphor.*" By M. O. FORSTER.

The dioximes of camphorquinone, three of which were described by Manasse (*Ber.*, 1893, xxvi., 243), have been obtained in purer condition, and the series of four completed. The following table summarises the chief characteristics of these substances:—

	M. p.	$[\alpha]_D$ in alcohol.	$[\alpha]_D$ in 2 per cent sodium hydroxide.	Precipitate with sodium hydroxide and ferrous sulphate.	C.c. of absolute alcohol at 20° required to dissolve 1 grm.
α-Dioxime ..	201°	−63·6°	−98·3°	Chocolate	40
β Dioxime..	248	—	−24·1	Chocolate	590
γ-Dioxime ..	135	+22·4	+12·6	None	1·0
δ-Dioxime ..	199	+75·5	+83·6	Chocolate	12·4

The *peroxide* of the dioximes, $C_{10}H_{14}O_2N_2$, obtained by oxidising them with potassium hypobromite, melts at 144·5°, and when reduced with zinc and acetic acid, yields the α-dioxime.

The *anhydride* of *iso*nitrosocamphor, $C_{20}H_{28}O_3N_2$, prepared by heating together the potassium and benzoyl derivatives of *iso*nitrosocamphor in benzene, is also formed when benzoyl chloride, acetyl chloride, phosphorus oxychloride, or acetic anhydride acts on the dry alkali derivatives. It melts at 187°, becoming transformed into the anhydride of α-camphornitrilic acid; a 2 per cent solution in chloroform has $[\alpha]_D$ +141·7°.

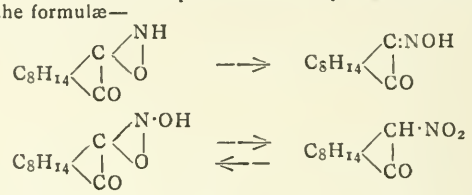
Two isomeric *compounds*, $C_{17}H_{18}O_5N_2$, melting at 136—137° and 152° respectively, are produced by the action of *m*-nitrobenzoyl chloride on an alkaline solution of *iso*nitrosocamphor. As in the case of the benzoyl derivatives, the substance of lower melting point is yellow, whilst the other is colourless. On hydrolysis, the former gives rise to a new modification of *isonitrosocamphor*, $C_{10}H_{15}O_2N$; this compound, which is still under investigation, melts at 114° and passes into the known isomeride between that temperature and 152°.

DISCUSSION.

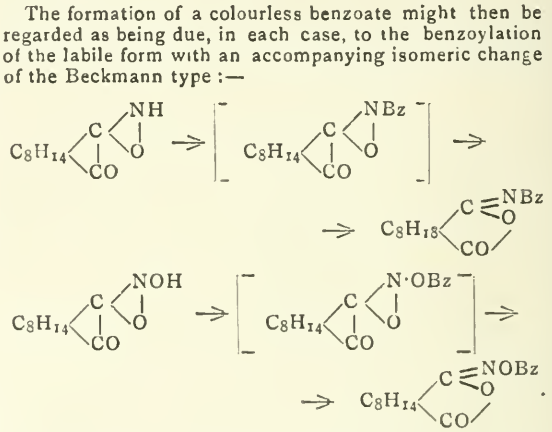
Dr. ARMSTRONG pointed out that if Dr. Forster's discovery of a yellow benzoyl*iso*nitrosocamphor were taken into account, together with Miss Whiteley's recent important observations on the colour of oximic compounds, the absence of colour from *iso*nitrosocamphor and the dioximes could only be explained—if they were regarded as true oximic compounds—on the assumption that they were polymerised molecules; but he was of opinion that it was premature, at present, to accept the explanation afforded by the Hantzsch-Werner hypothesis of the isomerism subsisting among the dioximes. On various grounds, he held this hypothesis to be open to grave question. Even the structure of camphorquinone appeared to be by no means placed beyond doubt.

Dr. SILBERRAD asked whether the benzoylation of camphor*iso*imide had been tried in perfectly dry pyridine in place of the alkaline solution used in the Schotten-Baumann reaction, and stated that this modification had proved very useful in the benzoylation of compounds which undergo immediate hydrolysis in contact with water.

Dr. LOWRY said that if the labile form of *iso*nitrosocamphor were regarded as an *iso*oxime, the isomerism described by Dr. Forster would correspond closely with that of the *normal* and *pseudo*-nitrocamphors, as is shown by the formulæ—



The formation of a colourless benzoate might then be regarded as being due, in each case, to the benzoylation of the labile form with an accompanying isomeric change of the Beckmann type:—



Dr. FORSTER stated that the molecular weight of the new *iso*nitrosocamphor had not been determined, but that as soon as the necessary material had been accumulated the general behaviour of the substance would be more closely studied; Dr. Silberrad's suggestion relating to camphor*iso*imide would be adopted.

*52. "*Reversibility of Enzyme or Ferment-action.*" By A. C. HILL.

It has been shown previously that the hydrolysis of maltose to glucose by yeast extract in concentrated solution is incomplete, the phenomena being due to polymerisation of the glucose by a reversible process, and a point of equilibrium is approached which varies with the concentration of the total sugar. In further publications, it was also pointed out that the polymerisation of glucose resulted in the formation of isomeric sugars, and somewhat different results were obtained when Taka-diastase and the pancreatic ferments respectively were used instead of yeast extract. In every case, it was possible, by diluting solutions of the synthetical products, to hydrolyse these compounds back to glucose by the enzyme used in their synthesis. Further, it had been found that the synthetical products of the action with yeast extract are hydrolysed by Taka-diastase, and those of the action with Taka diastase by yeast extract.

When the products of the synthetical change obtained by the use of yeast ferment, whilst still mixed with unchanged glucose, are fermented with *S. Marxianus*, only this hexose is fermented; but when a yeast containing maltase is employed, a part also of the synthetical product is fermented. Again, if the synthetical products in dilute solution are submitted to the hydrolytic action of yeast extract and then treated with *S. Marxianus*, the

whole is fermented. The sugar that is not fermented either by *S. Marxianus* or by yeasts containing maltase has been separated and proves to be a new biose, which is called *revertose*. The other sugar, which is fermented by all yeasts containing maltase, but not by *S. Marxianus*, is believed to be maltose, for although it has not been obtained pure, yet on fractionating mixtures of this sugar with revertose, specimens have been obtained in which the former sugar preponderates and of which the optical and other properties approach those of maltose. Its osazone crystallises in plates, whilst the corresponding derivative of revertose separates in needles. Revertose is formed in larger quantity, and the equilibrium point of glucose $\rightleftarrows$ revertose is more favourable to the synthetical change than the equilibrium point of maltose $\rightleftarrows$ glucose, which favours the hydrolytic reaction.

The products of the synthetical change with Taka-diastase are equally fermentable in part by all maltase-containing yeasts, and, as previously indicated (*Proc.*, 1901, xvii., 184), are readily re-hydrolysed by the same ferments in dilute solution. These products have not been separated.

Since the first paper on this subject (*Trans.*, 1898, lxxiii., 634), further observations of a similar nature have been made by the author and others, and the number of ferments for which a reversible action has been noted has become extended. These results warrant the adoption of the hypothesis that all ferment actions are reversible.

Discussion.

Mr. A. R. Ling said that recent experiments on the action of various hydrolytic enzymes on polysaccharides had shown that hydrolysis was invariably accompanied by a reversed or synthetical action, Dr. Hill being the first to notice that this reversion occurred when a concentrated solution of *d*-glucose is submitted to the action of yeast maltase.

In conjunction with Mr. B. F. Davis, he had obtained evidence that a certain amount of reversion occurred at a certain stage in the reaction between malt diastase and 3 per cent starch paste.

The use of the term "reversion" was, however, scarcely justifiable, as in no case had reversion led to the regeneration of the original carbohydrate, the products being *iso*-sugars, as had been shown in certain instances by E. Fischer and E. F. Armstrong. As it was extremely unlikely that the same product was obtained from a given carbohydrate by the use of different enzymes, the name "revertose" seemed too general for any specific compound obtained in this way.

Dr. E. F. Armstrong remarked that the important question to be decided with reference to the synthetical action of enzymes was whether the sugar synthesised was identical or not with that normally hydrolysed by the enzyme, and expressed the view that, at present, the experimental evidence tends to prove that the synthesised biose and the hydrolysed biose bear the same relation to one another as do the α- and β-methyl glucosides. He thought that the portion of the material fermented by yeast was more likely glucose than maltose, and did not consider the evidence sufficient to establish the individuality of revertose as distinct from the *iso*maltose proved by Emmerling to be formed by the action of maltase on glucose.

Mr. J. L. Baker enquired whether any derivatives of revertose other than the phenylosazone had been prepared, as, for example, the acetyl and benzoyl compounds. Was the evidence of the identity of revertose based solely on the physical constants and the osazone?

In reply, Dr. Croft Hill stated that revertose was obtained in white, crystalline, very hygroscopic crusts by dehydrating the vitreous mass in which it first separates from its alcoholic solution. It still contained a little ash, but the osazone was obtained quite pure.

Revertosazone is readily distinguished from Fischer's *iso*maltosazone by the fact that it is optically inactive, whereas Fisher's *iso*maltosazone was dextrorotatory.

The fermentation experiments with maltase-containing yeasts on the one hand, and with *S. Marxianus* on the other, were conducted on parallel lines, analyses being made at every step. The difference in the two cases could only be explained by the fact that in the former case a part of the synthetical product was fermented.

The view put forward by one school of chemists in Germany, that the action of ferments was not truly reversible, but that the substance synthesised is always different from the substance hydrolysed, is untenable, for in every case the synthesised substance can again be hydrolysed by the ferment which produces it.

He considered it likely that conditions of equilibrium may favour such a practical outcome, and the synthetical process in the organism may have such a relationship to the analytical process, but, theoretically, each component of the process is reversible in the strictest chemical sense.

*53. "*Discoloured Rain.*" By E. G. Clayton.

The rain which fell for some hours on Sunday, February 22nd, 1903, in all counties south of the Thames, and elsewhere, as at Clare in Suffolk, Oswestry in Salop, and on the Continent, as at Bochum in Westphalia, was turbid and discoloured, soiled window glass to an unusual extent, and left, on exposed surfaces, a greyish brown or terra-cotta-coloured deposit. The wind prevailing at the time was very high, and generally westerly or south-westerly. It has been suggested that the deposit was of volcanic origin, and probably due to the West Indian eruptions.

The following results were obtained with a specimen of the rain collected by Mr. R. Pound at Ashbury, near Shrivenham, Berkshire.

Chemical Examination.—After five days, the water remained opalescent, and yielded an extremely fine, light brownish red sediment:—

		Parts in 100,000.		Parts in 1,000,000.
(*a*).	Dissolved solids (dried at 150°)	25·1	Ammonia (free and saline)	0·95
	Dissolved solids (after ignition)	21·1	Ammonia (on boiling with alkaline permanganate)	0·15
(*b*).	Suspended matter	23·6		
	Chlorine	2·0		

The residue (*a*), after evaporation, blackened on ignition with an odour of burning wood, and, on further heating, the carbon soon disappeared. The inorganic matter was mainly calcium carbonate; alkaline chlorides and iron compounds being also present.

The suspended matter, which contained a mere trace of carbonate, was almost insoluble in dilute acids, but decomposed on warming with moderately concentrated sulphuric acid; its chief components were silica (67·5 per cent), alumina and ferric oxide (14·1 per cent), and volatile matter (12·4 per cent). The separated silica was perfectly white, and the volatile matter principally of organic origin.

The great differences between this specimen and ordinary rain water, especially as regards the proportions of chlorine, dissolved solids, and suspended substance, are sufficiently obvious.

Biological Examination.—One c.c. of the water, by plate cultivation on nutrient gelatin at 20—22°, yielded, by the fourth day, 420 bacterial colonies. Of these, 19 were non-liquefying iridescent expansions of irregular outline, having the characters of *Bacillus fluorescens non-liquefaciens*; the rest, which were sharply outlined circular pearly dots, resembled *Bacillus liquefaciens*, and began to liquefy the gelatin on the third day. After incubation for twenty-four hours at 38°, 1 c.c. of the water showed, in five days, only 33 bacterial colonies (*Bacillus subtilis ?*).

Microscopical Examination of the Sediment.—The particles, which range in size from 0·001 to 0·005 m.m., were yellow or brown, ressembling those of clay. This similarity was noticed by Prof. Bonney in a recently published letter describing some specimens of the deposit which he had received. In the sediment now under dis-

cussion, there were no vitreous, and very few angular, particles; between crossed Nicols prisms, the field was faintly illuminated. No pollen granules could be distinguished (although these appear to have been observed at Denchworth, Berkshire). The analysis, however, clearly indicates that some organic matter was present, both in solution and also in suspension in an exceedingly fine state of division.

The results show that this rain was charged with wind-borne dust, which in the specimen examined was a marly and ferruginous clay, mixed with organic refuse, perhaps of animal, as well as vegetable, origin; the calcareous matter had mainly dissolved in the water, which contained carbon dioxide, whilst the argillaceous and siliceous portions were carried in suspension. This composition is just such as might be expected in dust blown from the Jurassic and Cretaceous drift of Wessex roads and lanes. It is, therefore, not necessary to assume that the dust was conveyed either from remote regions or across the sea, and there are good grounds for supposing that, if a series of analyses had been made of the rain and sediment from different places, the figures would have reflected in some degree the local characteristics of the soils and subsoils of areas situated at a distance of a few miles, or even less, immediately to the west or south-west of those places. In a marly district, the ratio of calcareous matter to clay and silica would be high; where loam prevailed, fine siliceous sand would predominate; further west, felspar crystals and ferro-magnesian minerals would abound, possibly with less organic matter; from highly cultivated tracts, pollen granules might arise, and so on. Ashbury is situated partly on the Upper Greensand and partly on the chalk, and in the vicinity there are extensive areas of clay and chalk. An analysis by Mr. R. A. Earp (*Nature*, 1903, lxvii., 414) of matter deposited by the rain which fell on the same day at Buckfastleigh, Devon, showed that the sediment there contained less silica and more organic matter than the deposit examined by the author.

Discussion.

Dr. H. R. Mill said that he was investigating the fall of dust on February 22nd from a meteorological point of view in conjunction with Mr. Lempfert, of the Meteorological Office, and Mr. Clayton's theory of the local origin of the dust would be tested before long by the examination of fifty specimens obtained from rainfall observers and others in many parts of England and Wales, and some places abroad, this work having been undertaken by the Geological Survey. The magnitude of the dust-fall made it difficult to accept this hypotheses without very strong proof. In the south of England and in Wales, the dust, which was remarkably uniform in appearance, had fallen either dry or in rain over a space of 300 miles from west to east and 200 miles from south to north, whilst traces had occurred at intervals over the whole area of the British Isles from Scilly to Shetland. The fact that similar dust was observed on the same day over the greater part of the Channel Isles, Belgium, and Holland, and at many places in Germany, Switzerland, and Austria, as well as in the North Atlantic, whilst dust-storms prevailed off the coast of Africa, made a common origin seem very probable, and perhaps this was a case of far-travelled, wind-borne dust.

54. "*The Absorption Spectra of Nitric Acid in Various States of Concentration.*" By W. N. Hartley.

Photographs have been obtained of the spectra of nitric acid in eight different states of concentration, varying from 89·6 per cent of HNO_3 (sp. gr. 1·490 at 15°) to 20·31 per cent (sp. gr. 1·127 at 15°).

Acid of sp. gr. 1·490 transmits a very short spectrum, which is greatly lengthened by dilution. The acid of sp. gr. 1·432 (72·57 per cent) transmits a longer spectrum than the 20·31 per cent solution, but this is shortened on dilution; in like manner, weaker acids down to that of sp. gr. 1·127 behave in the same way, but here the dilute solution transmits a spectrum nearly as long as the strong acid. From this point onwards, an absorption band makes its appearance. If water acted simply as a diluent, dilution would cause an increase in the length of the transmitted spectra which would be proportional to the quantity of water added. There is evidently some chemical action between the water and the acid, but this action with acid of sp. gr. 1·490 is different from that with acid of sp. gr. 1·432 or any less concentrated acid. Hence it is probable that in strong nitric acid, the molecule is either polymerised to $n(HNO_3)$, or resolved into a compound of the nature of N_2O_5,H_2O. The acid of sp. gr. 1·490 might be represented either as a mixture, $N_2O_5,H_2O+H_3NO_4$, or as a compound, $H_3N_3O_9,H_2O$. The weaker solutions of the acid probably contain hydrates. Evidence is afforded that the strong acid contains two different substances, one of which acts on caustic lime whilst the other does not.

55. "*Salts of an Isomeric Mercaptoid Form of Thio-allophanic Acid, and a New Synthesis of Alkyl Imino-thiocarbamates.*" By A. E. Dixon.

By heating ethyl chlorocarbonate with phenylthiourea on the water-bath in presence of benzene, carbon dioxide was expelled and a yellow syrup formed, the latter being the hydrochloride of Bertram's (*Ber.*, 1892, xxv., 55) ethyl iminophenylthiocarbamate, NPh:C(NH$_2$).SEt or NHPh·C(NH)·SEt:—

$$NHPh\cdot C(NH)\cdot SH + EtO\cdot COCl = CO_2 + NHPh\cdot C(NH)\cdot SEt,HCl.$$

With methyl chlorocarbonate, under like conditions, the hydrochloride of methyl iminophenylthiocarbamate was obtained.

p-Tolylthiourea and methyl chlorocarbonate yielded the *hydrochloride* of *methyl imino-p-tolylthiocarbamate*, $NH(C_7H_7)\cdot C(NH)\cdot SMe,HCl$, in long, white prisms melting at 154—155°; the corresponding *base* could only be obtained as an oil. From *o*-tolylthiourea, by heating with methyl chlorocarbonate, a syrupy hydrochloride was produced; the corresponding free base, liberated by the cautious addition of alkali, crystallised from light petroleum in white lozenges melting at 101—102°.

Methyl iminoallylthiocarbamate, $NH(C_3H_5)\cdot C(NH)\cdot SMe$, was not precipitated by alkali from the aqueous solution of its hydrochloride; the *picrate* formed yellow, hair-like needles melting at 149—150° (corr.).

Thiocarbanilide, when heated with ethyl chlorocarbonate, affords a carbethoxy-derivative melting at 95°, which is non-basic, and appears to have the constitution $NHPh\cdot CS\cdot NPh\cdot CO_2Et$ (Seidel, *Journ. Prakt. Chem.*, 1885, xxxii., 262); the *methyl* homologue crystallises from alcohol in white needles melting at 105°.

Experiments conducted in the cold led to results entirely different from those just mentioned; thus, methyl chlorocarbonate, when allowed to remain in contact with finely-powdered, monosubstituted thioureas, gradually reacted, without evolution of gas, to form additive products; these substances, which dissolved freely in water, yielding very acid solutions, proved to be hydrochlorides. By neutralising with alkali, or even by prolonged boiling of their aqueous solutions, the acid could be readily withdrawn, thereby leaving crystalline solids, sparingly soluble in water, and melting, with decomposition, at relatively high temperatures.

The following compounds of this class are described:—

Methyl phenylthio-ψ-allophanate,—

$$NHPh\cdot C(NH)\cdot S\cdot CO_2Me,$$

brilliant prisms, m. p. 166—167° (corr.); *methyl p-tolylthio-ψ-allophanate*, $NH(C_7H_7)\cdot C(NH)\cdot S\cdot CO_2Me$, flattened, white prisms, m. p. 175—176° (corr.); *methyl o-tolylthio-ψ-allophanate*, colourless prisms, m. p. 175—176°) (corr.).

Thiourea itself also affords, with chlorocarbonates, two distinct classes of derivatives.

Ethyl thio-ψ-allophanate, $NH_2\cdot C(NH)\cdot S\cdot CO_2Et$, is

formed when thiourea and ethyl chlorocarbonate are very cautiously warmed in presence of benzene or, preferably, absolute alcohol, or by adding carbonyl chloride, in toluene, to thiourea suspended in absolute alcohol; its hydrochloride forms beautiful, transparent octahedra melting at 116—117° with effervescence, due to the escape of carbon dioxide; the fusion product a viscid syrup which appears to be identical with that obtained by heating thiourea with the chlorocarbonate, is the *hydrochloride* of *ethyl iminothiocarbamate*, $NH_2{\cdot}C(NH){\cdot}SEt$.

Methyl thio-ψ-allophanate, like the ethyl homologue, is readily soluble in water; its hydrochloride forms a white, crystalline powder, which melts at 89—90° with effervescence, and is thus converted into *methyl iminothiocarbamate hydrochloride*, $NH_2{\cdot}C(NH){\cdot}SMe,HCl$; this product, when obtained by heating thiourea and methyl chlorocarbonate in presence of benzene, separates as an oil, which subsequently changes to a crystalline solid melting at 59—60°. Both this and the corresponding ethyl derivative give mercaptan with cold alkali hydroxides, and yellow precipitates with alkaline lead and silver salts; the thio-ψ-allophanic compounds, on the other hand, yield no mercaptan with alkali, and are simply desulphurised by treatment with the metallic salts.

56. "*Derivatives of* o-*Aminobenzophenone and* p-*Aminobenzophenone.*" By F. D. Chattaway.

Considerable quantities of *o*-aminobenzophenone and *p*-aminobenzophenone having been prepared in an investigation of the transformation of dibenzanilide into these substances (*Proc.*, xix., 57), a number of their nitrogen halogen derivatives have been studied. These are formed by the action of aqueous hypochlorous or hypobromous acid on the acylaminobenzophenones dissolved in alcohol, but in order to obtain products that can be crystallised it is necessary to work at a low temperature and to guard carefully against any liberation of free halogen. The nitrogen halogen derivative can be extracted with chloroform, and re-crystallised from light petroleum or a mixture of this and the preceding solvent.

Acetyl-o-chloroaminobenzophenone, $Ph{\cdot}CO{\cdot}C_6H_4{\cdot}NClAc$, colourless, flattened prisms with domed ends, m. p. 102°; *acetyl-o-bromoaminobenzophenone*, $Ph{\cdot}CO{\cdot}C_6H_4{\cdot}NBrAc$, short, transparent, yellow prisms, m. p. 121°; *propionyl-o-chloroaminobenzophenone*, $Ph{\cdot}CO{\cdot}C_6H_4{\cdot}NCl{\cdot}COEt$, clusters of colourless, flattened prisms, m. p. 107°; *propionyl-o-bromoaminobenzophenone*, clusters of yellow plates, m. p. 90°; *benzoyl-o-chloroaminobenzophenone*, $Ph{\cdot}CO{\cdot}C_6H_4{\cdot}NCl{\cdot}COPh$, colourless, rhombic plates, m. p. 98°.

Acetyl-p-chloroaminobenzophenone, groups of colourless, slender, flattened plates, m. p. 124°; *acetyl-p-bromoaminobenzophenone*, groups of pale yellow, six-sided plates, m. p. 151°; *propionyl-p-aminobenzophenone*, colourless, elongated plates, m. p. 139°; *propionyl-p-chloroaminobenzophenone*, colourless, flattened prisms, m. p. 129°; *propionyl-p-bromoaminobenzophenone*,—

$$Ph{\cdot}CO{\cdot}C_6H_4{\cdot}NBr{\cdot}COEt,$$

pale yellow plates, m. p. 123°; *benzoyl-p-chloroaminobenzophenone*, clusters of colourless plates, m. p. 107°; *benzoyl-p-bromoaminobenzophenone*, clusters of yellow, rhombic plates, m. p. 93°.

The transformation which occurs when these substituted nitrogen chlorides and bromides are heated above their melting-points is accompanied by considerable decomposition, and dark, impure products are obtained. When the compounds are dissolved in acetic acid and warmed, the halogen passes from the nitrogen into the ring in the usual manner.

57. "*Action of Caustic Alkalis on Cinnamic Acid Dibromide and its Esters.*" By J. J. Sudborough and K. J. Thompson.

Good yields of α-bromocinnamic and α-bromo*allo*cinnamic acids may be obtained under suitable conditions by the action of caustic alkalis on cinnamic acid dibromide and its esters. The relative amounts of the two acids produced depend mainly on the employment either of the acid dibromide or of an ester, and, to a less extent, on the alkali and the solvent; the yield of α-bromo-acid (m. p. 131°) is always greater when an ester is employed. In no case has it been found possible to obtain only the normal product, namely, α-bromo*allo*cinnamic acid. The two acids are readily separated by the aid of their barium salts.

A by-product often obtained is ω-bromocinnamene, $CHPh{:}CHBr$, and this appears to be a primary decomposition product of the acid dibromide, and is therefore not obtained indirectly from one or the other of the α-bromo-acids, as stated by Barish. The addition of bromine to ethyl cinnamate and the transformation of the *allo*-acid into the α-bromo-acid have also been studied.

58. "*The Composition of Caro's Acid.*" By T. S. Price.

Amstrong and Lowry (*Proc. Roy. Soc.*, 1902, lxx., 94) have shown that, in dilute solution, Caro's acid is to be represented either by the formula $H_2S_2O_4$, assuming that the acid is dibasic, or by H_2SO_5 if the compound is regarded as monobasic. Since this conclusion is opposed to the results formerly obtained by the author (*Ber.*, 1902, xxxv., 292), a new series of experiments on the increase of acidity has been undertaken, and the revised data now agree with the results of these investigators, although the method employed in the author's experiments was less accurate.

The increase in acidity was formerly estimated by means of barium hydroxide solution, but Caro's acid, when neutralised by this alkali, is decomposed, 1 mol. of $H_2S_2O_9$ giving rise to 2 mols of H_2SO_4, so that the actual increase is twice the calculated quantity. If sodium hydroxide is employed, the acid is not decomposed, and the normal increase in acidity is indicated.

This difference in the behaviour of the two alkalis is also suggested by a determination of the ratio of iodine equivalent to increase in acidity, the mean values found being 4·74 and 2·75 for sodium hydroxide and barium hydroxide respectively. The deviation from the corresponding theoretical numbers (5·18 and 2·59) is probably due to experimental errors.

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

Ordinary Meeting, March 31st, 1903.

Mr. Charles Bailey, M Sc., F.L.S., President, in the Chair.

Mr. R. L. Taylor, F.C.S., read a paper entitled—I. "*On a Higher Oxide of Cobalt;* II. *A Method for the Volumetric Determination of Cobalt.*"

He stated that there appears to be a considerable number of higher oxides of cobalt—higher than the sesquioxide. The sesquioxide, indeed, is very seldom obtained by precipitation from solutions of cobalt. Mr. Taylor finds that the black oxide of cobalt, which is precipitated from an exactly neutral solution by calcium or barium carbonate in presence of bromine water, is fairly constant in composition, and may be represented as either Co_9O_{14} or Co_7O_{11}. Like the rest of the somewhat complicated oxides which have hitherto been described, it is probably a mixture or compound of the sesquioxide and the dioxide. As cobalt is completely precipitated in five to ten minutes by calcium or barium carbonate in presence of bromine water in a perfectly neutral solution, Mr. Taylor proposes to dissolve the precipitated oxide, after washing, in a mixture of hydrochloric acid and potassium iodide (Bunsen's method). Then, by determining the amount of iodine liberated, it is possible to find the amount of cobalt which was present. In calculating the result, the composition of the precipitated oxide is taken

as intermediate between the two given above. Before precipitation of the cobalt the solution must be free from iron, lead, and manganese. Nickel does not interfere. The volumetric process has been tested by Mr. J. H. Davidson, B.Sc. (Vict) in the assay of cobalt ores, with satisfactory results.

NOTICES OF BOOKS.

The Chemical Changes and Products Resulting from Fermentations. By R. H. Aders Plimmer, D.Sc.(Lond.). London, New York, and Bombay: Longmans, Green, and Co. 1903. Pp. 184.

In this volume the author deals seriatim with the chemical changes which are the result of the fermentation of the carbohydrates and the albumins. These changes are generally brought about by hydrolysis, but oxidation as well as reduction also takes place.

The carbohydrates are generally divided into four classes, viz., the polysaccharides, the trisaccharides or saccharotrioses, the disaccharides or saccharobioses, and the monosaccharides or monoses. These are each dealt with specially in the first six chapters.

Chapter XIII. is an interesting one; it is on the nitrification and denitrification taking place in the soil; it is known now that these processes of oxidation and reduction are the results of the action of several micro-organisms. Formerly it was thought that the change of ammonium salts into nitrates in the soil was a purely chemical reaction, but the results of the researches of several investigators, Frankland, Warington, and Winogradsky among others, showed that the action was a bacterial one, and took place in two stages. In the first stage the ammonium salts are converted into nitrites, in the second stage the nitrites are converted into nitrates. Other bacteria, again, have the property of liberating free nitrogen from these salts, and this is assimilated by another set of bacteria occurring in the roots of leguminoses, and converted into albuminous bodies. This short description may be taken as an indication of the general contents of this interesting book. Fermentation, changes in blood, in milk, in muscle, are all described, and the reactions made clear.

On page 141 the author sums up his principal deductions from the chemical changes occurring in fermentation as follows:—"1. That the active agent in all cases is a living organism. 2. That this organism sets up either by its own metabolism, or by bodies secreted by or excreted from it, changes in substances of different constitutions; *e.g.*, carbohydrates and albumins. 3. That these changes are principally hydrolytic, and that some are oxidative and a few reductive. 4. That the results of these changes are generally simplifications of the original body. 5. In certain cases synthesis occurs."

The book is well and carefully written, and contains much that is both useful to the specialist and interesting to the general reader.

There is a long bibliographical list of books and papers bearing on the subject, and two indices, one of authors' names, the other of subjects.

Elementare Voolesungen über Telegraphie und Telephonie. 3 Lieferung. ("Elementary Lectures on Telegraphy and Telephony," Part III.). By Dr. Richard Heilbrun. Berlin: Georg Siemens. 1902.

In the continuation of these elementary lectures on telegraphy and telephony the leading features of the previous volume are conspicuous. They bear the impress of the able and efficient teacher in the simplicity of the language employed, the fulness of explanation given, and, above all, in the way in which the difficulties, often only partly realised even by the students themselves, are forestalled. This volume contains the conclusion of the lecture on the chemical effects of currents, and a lengthy lecture on the production of currents, including the various modifications of cells and their arrangements in batteries, all very lucidly described, and illustrated by excellent explanatory diagrams.

Beiträge zur Chemischen Physiologie und Pathologie ("Contributions to Chemical Physiology and Pathology"). Edited by Franz Hofmeister. Band III. 11 Heft. Braunschweig: Friedrich Viewig und Sohn. 1903.

The most important paper in the February number of these *Beiträge* is one on "The Anaërobic Metabolism of the Higher Plants, and its Connection with Alcoholic Fermentation," by J. Stoklasa, Joh. Jelinek, and Eugen Vitek. This will be read with the greatest interest by all physiological chemists. The authors have examined the problems connected with the isolation of invertase, and believe that they have proved the presence of an enzyme in the juice of *Beta vulgaris*, which though possibly not identical with Buchner's zymase, at any rate has much in common with it. The paper describes in detail the authors' careful and painstaking researches, during the course of which important results have been obtained. Other articles in the number include a short paper on the composition of ovo-mucoid, by Leo Langstein, and another by A. Ostwald on the action of iodine on the protein substances.

Vorlesungen über Experimental Physik ("Lectures on Experimental Physics"). By August Kundt. Braunschweig: Friedrich Viewig und Sohn. 1903.

These lectures were delivered by the late Prof. Kundt in the years 1888-89, and have been prepared for publication by Dr. Karl Schiel. Though considerable advances have been made in the last fifteen years in the generally accepted methods of teaching an experimental science, it has not been thought advisable to make any additions to, or alterations in, these lectures lest their highly characteristic style should be thereby impaired. The text is prefaced by a short life of Kundt, and appreciation of his works by his brother-in-law, G. Schwalbe. The subjects of the lectures include the elementary principles of mechanics, heat, sound, electricity and magnetism, and optics, and the treatment throughout is such as to exclude almost entirely the use of even the most elementary mathematics, though in other respects it is very full, and likely to suggest to the teacher many useful ideas and methods in training the students' powers of induction. The book is not designed for use in the laboratory, and hence no practical details are included for performing the many experiments described. The pages devoted to sound exhibit most clearly the characteristics of the author, and will undoubtedly be found particularly attractive and stimulating. The illustrations and diagrams are copious throughout, and particularly clear.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 20—21.

Electric Conductivity of the Oximidocyanacetic Ethers.—P. Th. Muller.—The author finds that it is possible to calculate the infinite molecular conductivity of the sodic salts of these bodies by means of the Ostwald-Bredig law, which characterises them as distinctly monobasic acids; the nitroso-ethers behave just like ordinary carboxylised acids.

The Soda Salts of the Isonitrated Derivatives; a New Method for Diagnosing the Pseudo-acids.—P. Th. Muller.—Already noticed.

The Precipitation of Cupric Chloride and Bromide by Sulphuric Acid.—Georges Viard.—*Cupric Chloride.*—Sulphuric acid added in large excess to the solution drives off bubbles of hydrochloric acid, while the mixture becomes very hot, but the amount of chloride decomposed is very slight, and nearly all the dissolved salt is precipitated in the form of brownish-yellow anhydrous chloride. When the sulphuric acid is not in sufficient excess, the green hydrated chloride, $CuCl_2+2H_2O$, is precipitated. More than 68·4 per cent of its weight of sulphuric acid must be added for the anhydrous chloride to be formed. This anhydrous chloride appears as very small yellow crystals under the microscope; by allowing the green solution of $CuCl_2$ in H_2SO_4 to cool slowly, much more voluminous arborescent crystals are deposited. *Cupric Bromide.*—An excess of sulphuric acid precipitates this salt from its solution, but the precipitate always consists of the black anhydrous bromide. The reaction is much more sensitive than with the chloride, a solution of 1/200th $CuBr_2$ with an excess of sulphuric acid gave an abundant black precipitate. The difference of solubility of the chloride and the bromide in sulphuric acid furnishes a ready means for distinguishing between these two salts. A mixture of 1 volume of sulphate of copper at 1/10th with 10 volumes of H_2SO_4 is prepared in advance. By adding to this mixture a few drops of the salt to be tested a precipitate is formed; if yellow it is a chloride, if black it is a bromide. In this manner a solution of KCl at 1/100th, or of KBr at 1/200th can be recognised.

The Precipitation of the Chlorides and Bromides of Cadmium, Mercury, and Tin by Sulphuric Acid.—G. Viard.—Already noticed.

Improvements in the Use of Marsh's Apparatus.—A. Gautier.—Requires the accompanying drawing.

Condensation of Ethylic Alcohol with Œnanthylic Alcohol; Synthesis of Normal Nonylic Alcohol.—Marcel Guerbet.—If œnanthylic alcohol is heated with sodium ethylate, normal nonylic alcohol is produced according to the equation $C_7H_{16}O+C_2H_5ONa=C_9H_{20}O+NaOH$. The synthesis is effected best by heating the mixture obtained by dissolving 1·20 grms. of sodium in 8 grms. of œnanthylic alcohol, and 10 grms. of ethylic alcohol, to 230° in sealed tubes. Ethylene, hydrogen, acetic and œnanthylic acids, and alcohols, which can be separated by fractional distillation, are formed. The fraction coming over at 190—215° is rectified, and, finally, 8 grms. of an alcohol boiling at 212—214° is separated; this has the composition of normal nonylic alcohol, $C_9H_{20}O$.

Condensation of Œnanthylic Alcohol with Propylic Alcohol; Synthesis of Methyl-8-nonylol-9.—Marcel Guerbet.—The operation, conducted as in the last note, and using 100 grms. of œnanthylic alcohol and 250 grms. of propylic alcohol, gives 18 grms. of an alcohol boiling at 221—223°, having the formula $C_{10}H_{22}O$. This decylic acid is an oily colourless liquid with an odour of tallow, boiling at 261—265°; its constitution is found to be $CH_3.(CH_2)_6.CH(CH_3).CO_2H$, and that of the corresponding alcohol is $CH_3.(CH_2)_6.CH(CH_3).CH_2.OH$.

Action of the Chlorides of the Fatty Acids on the Soda Derivatives of the Acetylacetic Ethers.—L. Bouveault and A. Bongert.—The authors describe the preparation of sodacetylate, the action of the acid chloride on the soda derivative, the separation of the two isomerous acylised derivatives, and the acid chloride derivatives of high and low molecular weights.

The O-acylised Derivatives of the Acetylacetic Ethers and their Decomposition.—L. Bouveault and A. Bongert.—These bodies are true ether salts of the enolic compound isomerous with acetylacetic ether; that is to say, β-oxycrotonic ether. A number of these derivatives are described. Water is without action on the *o*-acylised derivative, even in sealed tubes at 140—150°. Aqueous ammonia decomposes the *o*-butyrylacetylacetate of methyl into butyrate of ammonium and acetylacetate of methyl, but dry ammonia gas gives butyramide and β-amidocrotonate of methyl, by reason of its subsequent reaction on the regenerated acetylacetate of methyl.

The Formation of Trioxymethylene by the Direct Oxidation of the Aromatic Compounds of the Metho-ethylenic Chain.—M. Tiffeneau.—Under the influence of slow oxidation in contact with the air, the aromatic compounds of the metho-ethenylic chain, $R-C\equiv\begin{matrix}CH_2\\CH_3\end{matrix}$, give rise to formic aldehyde, which is deposited in the form of trioxymethylene on the sides of the flask in which it is contained. It is isolated by filtration, washing with ether and desiccation, and commences to sublime slowly at 100°; it fuses at 160°. It is insoluble in the ordinary solvents, but completely soluble in ammonia, with the formation of hexamethylene-tetramine, which can be isolated by evaporating the ammoniacal solution *in vacuo*.

Presence in the White of Egg of a Fibrinogenous Substance which is Transformed "in vitro" into Semiorganised Membranules.—A. Gautier.—There exists in egg albumin from hen's eggs (and probably in those of other birds) an albumenoid substance to which the name *ovofibrinogen* is given; it is analogous to the fibrinogen of the blood or to the myosimogen of living muscle; 1·5 per cent of ovofibrinogen is found in dry egg albumin. Solution in water, heat, or alkalinity, conditions which assist the action of cellular animal ferments, favour also the transformation of ovofibrinogen into ovofibrin.

MISCELLANEOUS.

Action of Baryta and of Sodium on the Aldehydes.—Anton Lederer.—Concentrated solutions of baryta react with acetaldehyde and crotonic aldehyde, resinifying them. Isobutylic aldehyde, heated with baryta water in a sealed tube to 150°, gives a mixture of alcohol and isobutyric acid. That is to say, it constitutes an exception to the rule previously announced (*Bull. Soc. Chim.*, vol. xxviii., p. 477), as the neighbouring carbon of the CHO, in this case, still contains an atom of hydrogen. Under the same conditions isovalerianic aldehyde simply undergoes condensation, giving α-isopropyl-β-isobutylacrolein, already described by Kohn (*Bull. Soc. Chim.*, vol. xvi., p. 1630). Sodium reacts vigorously on isobutylaldehyde; during the reaction a little isobutylic alcohol is formed, as well as isobutyrate of octylglycol. This latter is characterised by its saponification with potash alcohol, which separates it into Fosser's octylglycol, fusible at 51—52°, and isobutyric acid. It appears that the sodium only reacts through the soda formed by the small amount of moisture present; in fact, powdered caustic soda gives the same results. In the same manner, with isovalerianic aldehyde we obtain the corresponding valerianate of glycol.—*Mon. f. Ch.*, vol. xxii., p. 536.

MEETINGS FOR THE WEEK.

Monday, 27th.—Society of Arts, 8. (Cantor Lectures). "Mechanical Road Carriages," by W. Worby Beaumont, Mem.Inst.C.E.

Tuesday, 28th.—Royal Institution, 5. "The Blood and some of its Problems," by Prof Allan Macfadyen, M.D., &c.

—— Society of Arts, 7 30. (Applied Art Section). Visit to the Whitefriars Glass Works. "Modern Table Glass," by Harry Powell. (Special Tickets required).

Wednesday, 29th.—Society of Arts, 8. "Automatic Wagon Couplings on British Railways," by T. A. Brockelbank.

Thursday, 30th.—Royal Institution, 5. 'Hydrogen—Gaseous, Liquid, and Solid,' by Prof. Dewar, F.R.S., &c.

Friday, May 1st.—Royal Institution, 9. "Recent Advances in Stereo-chemistry," by Prof. W. J. Pope, F.R.S.

—— Royal Institution, 5. Annual Meeting

Saturday, 2nd.—Royal Institution, 3. "The Early Art of Siena," by Prof. Langton Douglas, M.A.

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THE CHEMICAL NEWS.

VOL. LXXXVII., No. 2266.

A SIMPLE INSTRUMENT FOR MECHANICALLY CALCULATING THE WEIGHT OF VITRIOL IN CHAMBERS.

By C. DAVIDSON.

THIS instrument is very simple, both as regards materials and construction, and may easily be put together in a few hours by anyone possessed of a little skill in draughtsmanship; although, like most mechanical calculators, it is rather difficult to describe in words. The only mathematical principle involved is that of the proportionality of the sides about the equal angles in similar triangles—which is understood by everybody.

According to the usual formula, the weight in tons of the actual "oil of vitriol" in a chamber is given by the equation—

$$W = \frac{lbd}{12} \cdot \frac{62{\cdot}5}{2240} \cdot \frac{S\,P}{100}.$$

Where l is the length of the chamber in feet; b, its breadth, also in feet; d, the depth of acid in inches; S, the specific gravity of the acid; and P the percentage of oil of vitriol it contains.

For convenience of calculation, the right-hand member in usually written in the form—

$$d\left(\frac{62{\cdot}5\,l\,b}{12 \times 2240}\right)\frac{S\,P}{100}.$$

The value of the part within brackets is then calculated, once for all, for each chamber in the works, the series of values for the various chambers is tabulated, and a similar table of values of S P/100 from 70° Tw. to about 140° Tw. is also made out. The calculation of the stock of vitriol in a chamber is then reduced to a multiplication of three numbers.

For this operation a slide-rule with two slides would serve very well; and indeed if, instead of being marked as usual with scales of numbers, the graduations on the rule were made to correspond with the values of the above-mentioned expressions, and were marked accordingly, it would be difficult to imagine anything more convenient in the actual working. Such a slide-rule, however, would be rather expensive, and its construction is certainly beyond the skill of most men. The use of an ordinary slide rule in conjunction with tables of reference is much less satisfactory than the instrument to be described.

Notice first that if from the expression for W the factor S P/100 is left out, the result is the *weight in tons of a volume of water equal to that of the acid in the chamber.* This weight we shall call w, the weight of the acid itself being W. Our first proceeding, then, is to find w.

For simplicity, consider a single chamber, and let the value of $\frac{62{\cdot}5\,l\,b}{12\times2240}$ for such chamber be C_1; then we have $w = dC_1$, which is the same as $\frac{w}{C_1} = \frac{d}{1}$.

Consider Figure 1. The angles, O M P, O A B, are right; it follows that $\frac{M\,P}{O\,M} = \frac{A\,B}{O\,A}$. If, then, O B be a thread fixed at O, but otherwise movable in the plane of the paper, and if A B be a scale of equal parts representing depths of acid, then on moving the thread O B so as to intersect A B at any particular graduation, the length cut off on M P will give, when measured according to the proper scale, the value of the weight w.

To pass from this to the actual weight of oil of vitriol in the chamber requires only a second application of the same principle.

$W = w \cdot \frac{S\,P}{100}$; or, putting $\frac{S\,P}{100} = C_2$, $W = wC_2$. This may again be written in the form $\frac{W}{C_2} = \frac{w}{1}$. So that, by means of an additional scale graduated for the values of C_2, the weight W may be obtained.

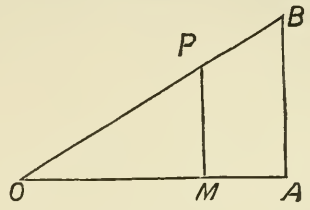

FIG. 1.

The details of construction and the fixing of proper values for the units will best be understood by considering a particular case. In a set of five chambers, the values of the expression $\frac{62{\cdot}5\,l\,b}{12 \times 2240}$ were as under:—

TABLE I.

No. 1	5·85
„ 2	7·25
„ 3	6·04
„ 4	6·04
„ 5	4·07

The values of the expression S P/100 for acids of 70—145° Twaddel are given in Table II., which is calculated from that in Lunge and Hurter's "Alkali Makers' Pocket-book."

TABLE II.

70°	0·606	108°	0·976
71	0·615	109	0·987
72	0·624	110	0·997
73	0·634	111	1·007
74	0·644	112	1·017
75	0·653	113	1·027
76	0·663	114	1·038
77	0·672	115	1·048
78	0·682	116	1·058
79	0·692	117	1·069
80	0·701	118	1·079
81	0·711	119	1·089
82	0·721	120	1·100
83	0·731	121	1·110
84	0·741	122	1·120
85	0·751	123	1·131
86	0·760	124	1·142
87	0·770	125	1·152
88	0·780	126	1·163
89	0·790	127	1·173
90	0·799	128	1·183
91	0·809	129	1·194
92	0·819	130	1·205
93	0·829	131	1·215
94	0·839	132	1·225
95	0·849	133	1·235
96	0·858	134	1·246
97	0·868	135	1·256
98	0·878	136	1·267
99	0·887	137	1·278
100	0·897	138	1·289
101	0·907	139	1·300
102	0·917	140	1·312
103	0·926	141	1·323
104	0·936	142	1·334
105	0·946	143	1·345
106	0·956	144	1·357
107	0·966	145	1·368

To construct the instrument, paste a sheet of damped paper (34 inches by 24 inches, or thereabouts) on a good drawing-board, well secured against warping, and having one long edge accurately straight.

When the paper has become thoroughly dry, draw a line, O A, about 3 inches from the straight edge of the board, and parallel to it. Take O about 4 inches from the left-hand side, and make O A about 20 inches long. At A draw A B, the line of "dips," perpendicular to the edge of the board, and about 20 inches long (Fig. 2). In the case

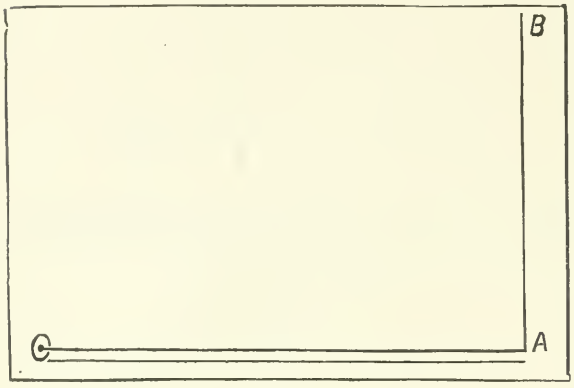

Fig. 2.

of the chambers mentioned above, the maximum depth of acid allowable is 25 inches; A B is therefore divided into 25 equal parts, and these are numbered 1 to 25, starting from A as zero. Each part is then subdivided into ten equal parts, and the scale is inked in.

tonnage of water per inch in each chamber—as given for the present case in Table I.—are laid down on a line drawn a quarter of an inch below O A and parallel to it, as shown. A separate line of this sort is graduated thus for each set of chambers, and the name or number of each chamber set at its own mark.

The values in Table II., being common to all the chambers, are laid down on O A itself, with the aid of the provisional scale already made. In order, however, to have the unit of the Twaddel scale of the most convenient size for working with, the values in Table II. are multiplied by 5, and the lengths on the scale corresponding to the products are marked off on O A. (The original scale may with advantage be inked in lightly on the under-side of O A; the Twaddel graduations being on the upper side. If this is done, any new chamber which may at a future time be added to the plant can have its graduation set alongside the others at once). These graduations are marked with the number of degrees Twaddel to which they correspond, and the scale is inked in.

Examination of Table II. will show that for acid at 110·3° Tw., SP/100=1.

At this point on the Twaddel scale on O A, erect another line perpendicular to the edge of the board. This is to carry a scale of equal parts, the unit for which we now proceed to find. Suppose we had 13·8 inches of *water* in chamber No. 2 above; this would weigh very nearly 100 tons. Join O to the 13·8 inch mark on A B, and from the mark for chamber No. 2 draw a line, perpendicular to O A, cutting the line last drawn. *The length of the vertical line intercepted between* O A *and the slanting line represents* 100 *tons.* Divide this line into ten equal parts, and extend the line to the top of the paper, continuing the graduations. Bevel the left-hand side of the T-square (the side which has been used for ruling these lines) till it is fairly thin at the edge, place it along this scale (keeping the stock against the edge of the board), and copy the scale on to

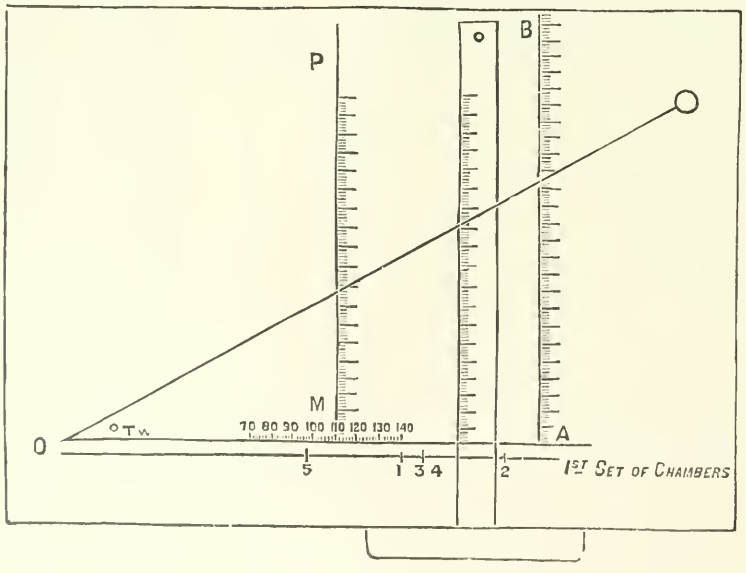

Fig. 3.

The values of the other two factors in the expression for W are laid off on lines parallel to O A. First of all, O A is divided into fifteen equal parts, and provisionally numbered, starting from O as zero, so that *two*-fifteenths of the total length is the unit; the figure at A being therefore 7·5. A O is then produced to unit length beyond O, and this last unit is divided into one hundred equal parts. By means of the scale so got, the values representing the

the T-square. Mark the graduations 0, 10, 20, &c., beginning at O A. Sub-divide each graduation into ten parts. Now slide the square along to the line drawn from the 110·3° Tw. mark, and copy the scale on to that line.

Fix one end of a strong thin silk thread at O, by looping it round a drawing-pin, and pass the other end of the thread (which is long enough to reach to the mark 25 on A B) up through a small hole in a thick circular piece of

lead heavy enough to keep the thread taut when placed so at any mark on A B. Fix the thread to the lead, and the instrument is complete, having the appearance shown in Fig. 3.

As an example of the working, let us suppose that we have 16·3 inches of acid at 126° Tw. in No. 1 chamber above. To find what this amounts to in tons of actual oil of vitriol, we set the thread to 16·3 on the line of "dips," slide the square along to the mark for No. 1 chamber, and read where the thread crosses the scale on the square; it will read 95·4. The thread is now moved to 95·4 on the scale M P, and the square slid along to 126° Tw. The reading at the point where the thread crosses the square now gives the weight of oil of vitriol in tons (110·9 tons).

It takes the most of an afternoon to graduate the instrument, but the saving of labour effected by it is considerable. Stocks may be calculated by it to within one-fifth of a ton more quickly (and *very* much more comfortably) than by means of logarithms; and the apparatus possesses the further advantage of requiring no reference whatever to tables of any kind. All the data required are on the instrument itself.

The author knows of works at which the oil of vitriol contents of a set of chambers are carefully calculated out to the nearest quarter of a hundredweight; that is so much energy wasted. The variation in strength of acid in a chamber from point to point is such that one must be satisfied with much less imposing figures.

37, Herriet Street, Pollokshields, Glasgow.

THE STRUCTURE OF SPECTRA.*

By Prof. CH. FABRY.

All those who have worked with the spectroscope, no matter how little, have had the opportunity of observing the magnificent spectacle offered by the spectrum of certain metals, such as that of iron, for example. But, to the feeling of admiration produced by the richness of the colours, the number and variety of aspect of the groups of lines, there is soon added, in the case of the attentive observer, a feeling of astonishment and uneasiness; all these brilliant lines, though emitted by the same vapour, seem to be thrown, haphazard, in all parts of the spectrum, as though by some capricious will without any systematic arrangement.

In other less complicated spectra, the eye seems to perceive some sort of regularity; but this appearance of orderly arrangement nearly always disappears when we endeavour to translate it into numerical relationships.

These lines of the same spectrum, so different in appearance and so irregularly distributed, have, however, a common origin, and it is difficult to admit that this progenitor, so to speak, does not show itself by some numerical relationship between their wave-lengths, or, in other words, between their positions in the spectrum. Such relationships have been searched for from the earliest days of spectroscopy. Though the first observations go back more than thirty years, it is only during the last fifteen years that this study has given rise to a slightly more extended collection and compilation of results, and there remains much more to be done before the observations are complete.

In the case of some spectra (those of the alkaline metals, for example), all the lines have been classified in a regular manner; the metals of the same family have analogous spectra, which are modified in a progressive manner as their atomic weights increase. With other metals, one part only of the lines shows any regular arrangement, and the others retain their arbitrary positions. Certain very complicated spectra, again, seem to escape all law.

* *Revue Générale des Sciences*, Year XIV., No. 5, March 15, 1903.

But in spite of all this, the results obtained up to the present form a very important collection, and it is these results that I propose now to examine.

I. *The Numerical Data.*

Each line in a spectrum shows the presence of a certain kind of monochromatic light in the radiation under examinination, or, in other words, a certain vibration of known period or wave-length. A line thus should be defined, not by a vague indication of colour nor by an arbitrary number on the scale of the spectroscope, but by the only element that can define it independently of all convention, the period of its vibratory movement, the number of vibrations taking place per second. According to an expression borrowed from the language of electricians, this number may be called the frequency of the vibratory movement under consideration. We know that in optics these numbers of vibrations are shown by millions of millions per second; they cannot be counted but only calculated, starting from the speed of propagation, V, which is very great, and the wave-length, λ, which is very small; the frequency, N, is then given by the equation $N = \frac{V}{\lambda}$, and the period by $T = \frac{\lambda}{V}$.

The speed, which is very difficult to measure, is not known closer than to a thousandth, but it is rigorously the same for all radiations, at least it is so *in vacuo*. On the other hand, the wave-lengths can be measured with extreme accuracy. As λ is simply proportional to T (V being constant), it is more simple not to bring the uncertainty of V into the numerical data of spectroscopy, and to define each radiation by its wave-length. These wave-lengths being very small, we measure them with a unit of the same order. We shall employ the thousandth of a micron, or the millionth of a millimetre (abbreviated, $\mu\mu$).*

The periods are directly proportional to the wave-lengths, and the frequencies are inversely proportional to them. We can take as a measure of the frequency the number of wave-lengths in a given distance, a tenth of a millimetre, for instance. In this manner we can express the number of vibrations occurring in a time which is perfectly determined, but imperfectly known, which gives the speed of light for a tenth of a millimetre as $\frac{1}{3} \times 10^{-12}$ second.

In short, the numerical data of spectroscopy consists of wave-lengths of the rays which compose the different spectra. The determination of these measurements has become comparatively easy, thanks to our knowledge of a large number of *datum* points in the spectrum. If they are sufficiently numerous, and if their wave-lengths are known exactly, it becomes an easy matter to determine the wave length of any given line by interpolation between two datum points which flank it, and this can be done, no matter what kind of spectroscopic apparatus is used. It must be borne in mind, however, that all errors in the datum points are repeated in the measurements deduced from them. The establishment of these fixed points has been a very laborious undertaking, and the names of Angström and Rowland stand out distinctly in connection therewith. All the modern numerical data are reduced to the figures of this latter worker; there are certainly numbers of small systematic errors, as has been pointed out recently by M. Perot and myself; but these errors are only in millionths, at least in the visible spectrum. We

* No international agreement has been come to yet on the choice of a unit for the measurement of wave-lengths. Most spectroscopists use the ten-thousandth of a micron (Angström's unit). That is not a matter of very great importance, since it only requires the moving of the decimal point. The use of $\mu\mu$ has this advantage, that the whole numbers of the usual wave-lengths are numbers of three figures, which are more easy to remember and repeat than those of four figures. For spectroscopic requirements, we should always give wave-lengths *in vacuo*, as they alone are exactly proportional to the periods of vibration. Experiment gives directly wave-lengths in the air; reduction to *vacuo* requires only a small correction, of which the calculation is easy with the help of the index of air.

have drawn up a table by which they can be corrected, but these corrections will be, as a rule, useless, as spectroscopic measurements can rarely attain this degree of precision. Thus, we may state, that for the usual kind of spectroscopic measurements Rowland's datum points are sufficient, but we can, if necessary, correct the figures obtained by their means.

When we reflect that the lines of certain spectra are to be counted by thousands, we get an idea of the enormous amount of work necessary to establish the numerical data of spectroscopy, and there is no need for astonishment that this work is not yet completed, in spite of prolonged researches, among which may be mentioned those of Kayser and Runge. The work is still increased by the fact that many substances give several spectra, according to the manner in which their vapour has been rendered luminous. The extreme sensitiveness of spectroscopic reactions further complicates the problem; if a trace of impurity is present in the body under examination, lines will be attributed to this substance which do not belong to it. Extremely great care and attention is necessary to prevent errors of this kind. Finally, for each line it is necessary to have a series of observations as to its properties, besides its wave-length; such as its width, brightness, appearance under varying circumstances of production, the manner in which it behaves under the influence of a magnetic field, or under the influence of increasing pressure of the surrounding medium, &c.

The compilation of these facts appears to be at first sight a useless and ungrateful task; but what follows will show that this is not the case at all, and that, as often happens, simple but important laws are found from accumulations of figures which have been collected simply through a love of exactitude.

II. *Doublets and Triplets at Constant Intervals.*

A comparison between the phenomenon of the emission of light and that of the production of sound occurs naturally to the mind, although the analogy is perhaps very far-fetched. But, admitting this comparison as legitimate, there is nothing any more surprising to see a gas emit several different luminous vibrations at one time than to hear a vibrating cord give at the same time its fundamental note and its different harmonics; the movement of the cord is a fairly complex periodic movement, which may be regarded as the superposition of a certain number of sinusoïdal movements, each of which corresponds in acoustics to a simple sound and in optics to a monochromatic light, and, consequently, to a definite spectral line. Now, in most of our musical instruments the different sounds emitted simultaneously obey the law of harmonics; their frequencies are as successive whole numbers. Depending on a mistaken analogy, we looked for analogous relations between the numbers of the vibrations of the movements emitted by a given luminous gas. We thought we had found some, generally only roughly approximate.

Recent researches have shown that these were only accidental. Certain spectra have such a large number of lines that we can find, with patience, all the numerical laws we wish to, always provided that the law sought for is only to apply to a small number of lines, and that we are contented with a slight degree of approximation. But the analogy upon which this preconceived idea was based was purely imaginary; even in acoustics movements which obey the simple law of harmonics are of rare exception; the limited powers of our ear have obliged us to choose our musical instruments in this exceptional category; we see no reason why the vibratory systems which emit light should belong to this category. Of the constitution of these systems we know nothing *à priori*. Only the study of facts undertaken without any preconceived ideas can teach us anything about the laws which connect the radiations given off.

The first well-founded fact was shown by M. Mascart in 1863; certain groups of lines of characteristic appearance are found repeated several times in the spectrum of the same metal. For example, magnesium gives a beautiful group of three fairly closely placed green lines, of which the wave-lengths are 518·38, 517·29, and 516·75. This triplet occurs several times with identical aspects in different parts of the spectrum of magnesium. M. Mascart found it three times in the ultra-violet, and now we know of fourteen examples, one in the infra-red, one in the visible spectrum, and twelve in the ultra-violet. Sodium gives a yellow doublet, known universally as the D line (lines D_1 and D_2 in the solar spectrum). Similar doublets occur twelve times in the sodium spectrum.

Although here we are dealing only with qualitative relationships, there can be no question of groupings due to chance; the probability of accidental triple groupings, like those in magnesium, is practically non-existent.

If we place these groups on a scale of wave-lengths (such as the spectra given by a train of prisms), we find that they are not all of the same dimensions; they become narrower as we advance towards the ultra violet. A simple change in the method of representing the spectrum suffices to show the existence of a numerical law. Instead of representing each line by its wave length, let us represent it by its frequency, and let us draw the spectrum according to these new numerical data. This change has the effect of expanding to some extent the region of short wave-lengths; that is to say, that portion where the groups were the narrowest. All the groups of the same metal (Mg or Na) become identical, and absolutely superposable. These groups, which are easily seen in the spectra of Mg and of Na because they are very narrow, do not become confused, but are seen as distinct elements. The same is no longer the case when the groups are sufficiently wide to become entangled or confused one with the other. The numerical law once found in two particular cases, it becomes possible to look for analogous groupings in the spectra of other metals. Let us represent each line by its frequency, and on the spectrum thus drawn (or better still, on the numerical data themselves), we look for groups with the same dimensions repeating themselves several times. Such groups have been found by Rydberg, then by Kayser and Runge, in the spectra of a large number of metals.

The alkaline metals give, like sodium, spectra composed of doublets; the same is the case with copper and silver, metals which are placed next to the alkaline ones in L. Meyer's classified list.

The divalent metals (Mg, Ca, Sr, Zn, Cd, Hg) give triplets; the same is the case with the metalloids O, S, and Se. All these triplets are not formed of equidistant lines; going from the red towards the violet, the first interval we meet with is always narrower than the second. In several of these bodies the triplets are so wide and so confused that simple observations, without precise numerical data, would not enable us to recognise them (such is the case with the mercury spectrum).

Here is, therefore, an extremely simple primary law; to which we may perhaps with justice give the name of Rydberg's law:—In the spectra of a large number of bodies exist groups (doublets or triplets), which occur several times over; the interval which separates the lines (on the scale of frequencies) is the same for all the groups.

Further, this is not a law, more or less roughly approached; but the constancy of the intervals when we pass from one group to another, is verified with a precision equal to that of the measurements.

For certain metals the groups thus put in evidence offer a number of curious characteristics to which we shall return later on.

With bodies that give doublets we shall have to determine a fundamental constant, viz., the constant interval between the two lines of the doublet. We shall have two constants for substances with triplets; the interval from the first to the second, and that of the second to the third. It is interesting to compare together the constants of bodies of the same family. As the atomic weights become

greater the constants increase; that is to say, the groups become wider. For the alkaline metals the width of the doublets (expressed, of course, by difference of frequencies) varies with the squares of the atomic weights; this is shown in the following table:—

Metal.	Atomic weight. P.	Width between doublets. v.	$\frac{v}{P_2} \times 10^4$.
Li*	7	—	—
Na..	23	0·17	3·25
K	39	0·57	3·81
Rb..	85	2·34	3·22
Cs..	133	5·45	3·09

Although the numerical law may not be as simple in other families, the sense of the variation of the width of the groups is always the same.

Let us show, finally, that in the case of the alkaline metals, besides these doublets with constant intervals, there exist others which also form a natural family, and which are closer and closer together as we advance towards the smaller wave-lengths. They will be dealt with in the next section; they form the principal series of the spectra of these metals.

(To be continued).

ON THE

ACTION OF HYDROGEN MONOSULPHIDE ON TELLUROUS AND TELLURIC SOLUTIONS, WITH SOME NOTES ON THE SULPHIDES OF TELLURIUM.

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IN the course of an enquiry into the various precipitation processes which have been devised for estimating tellurium, in which I have been engaged for some time past, and which has furnished the subject-matter of several communications to the CHEMICAL NEWS, I found occasion to further investigate chiefly from an analytical standpoint the action of H_2S on solutions of tellurium—tellurous and telluric—under varying conditions, and also to examine the precipitates thereby formed, with the object of assisting to clear away some of the doubt still apparently existing with regard to their exact character. The results of this work, being somewhat difficult of incorporation in either of my previous contributions, I have considered sufficiently interesting to be embodied in a separate communication.

Becker (*Liebig's Ann. Ch.*, xxx., 257—268), and, later, Brauner (*Journ. Chem. Soc.*, lv., 382—411), have shown that the statement originally made by Berzelius (*Pogg. Ann.*, viii., 411), and still to be met with in most of our text-books, that the precipitates obtained by the action of H_2S on solutions of compounds of TeO_2 and TeO_3 respectively are the sulphides corresponding to these oxides needs some qualification. This is made even more evident by the results of my own experiments.

(*a*). *Action of* H_2S *on Tellurous Solutions.*

The reddish brown precipitate which is at first formed when H_2S acts upon an acid tellurous solution quickly darkens, and, by the time the precipitant is present in excess in the liquid, becomes black and loses its flocculency. The brown precipitate is undoubtedly TeS_2, which, however, being very unstable, immediately dissociates, resolving itself almost entirely into a mixture of tellurium and sulphur, from which the latter element can be easily extracted by CS_2, with the exception of a small percentage which resists the action of the solvent and remains behind seemingly in combination with tellurium. It is stated by Becker that the proportions in which the elements occur in the precipitate are always "approximately" those required for TeS_2.

The H_2S precipitate when first formed readily dissolves in ammonium sulphide, and on this fact was based an early method of separating TeS_2 from the sulphides of lead, copper, bismuth, and other metals which are insoluble in that reagent. By digesting the mixed sulphides in the $(NH_4)_2S$ the TeS_2 was supposed to pass completely into solution as ammonium thiotellurite, and from this it was re-precipitated by the addition of dilute HCl (or other suitable acid), oxidised by HCl and $KClO_3$, and the tellurium finally precipitated by the sulphite or other process. In practice, however, this method proved a failure, it being found impossible to effect anything approaching complete separation of the elements, owing no doubt to the dissociation of the TeS_2 first thrown down in the mixed precipitate, the tellurium being then practically insoluble in the alkaline sulphide.

The tellurous solution used in the experiments described below was prepared by dissolving 2·3990 grms. of pure TeO_2 in HCl, and making up to 250 c.c. with water, so that each 50 c.c. taken contained 0·3798 grm. of Te.

Experiment A.—50 c.c. mixed with 200 c.c. freshly made H_2S water, thoroughly shaken, and the mixed solution (contained in a closed vessel) allowed to stand for several hours before being filtered. The precipitate was well washed first with water, and filtered as dry as possible; it was then repeatedly treated with absolute alcohol, and finally extracted with CS_2. The residue left after these operations was dried in a current of CO_2 at 105—110°, and was found to weigh 0·3899 grm., but after being maintained at 250° for three hours its weight diminished to 0·3809 grm., theory for Te being 0·3798. This loss, due to the volatilisation of sulphur insoluble in CS_2 and assumed to be in combination with tellurium, is equal to 2·314 per cent, or 6·870 per cent, of undecomposed TeS_2 in the original precipitate.

Experiment B.—The same volume of solution was taken as in A, and the method of procedure was in every respect similar, only that the extraction with CS_2 was omitted. The precipitate, after drying in a stream of CO_2 at 105—110°, weighed 0·5737, the calculated weight for TeS_2 being 0·5718. By treatment with CS_2 the sulphur was then extracted, and the residue found to consist of practically pure Te, the quantity of insoluble sulphur present being infinitesimal. Thus it would appear that the TeS_2 present in the moist precipitate is in great part dissociated in the process of drying at 105—110°.

Experiment C.—The 50 c.c. of solution diluted to 100 c.c. was saturated with H_2S by passing the gas through it, and the precipitate treated as in A. The insoluble sulphur found in the precipitate was equivalent to 6·986 per cent TeS_2.

Experiment D.—In this case the manner of precipitation was identical with that in A and B, only the precipitate was allowed to remain in contact with the H_2S solution in a closed vessel at a temperature of 75—85° for forty-eight hours before being filtered off, and treated as in A. The insoluble sulphur found corresponded to only 0·958 per cent TeS_2 in the original precipitate.

From these experiments, the details of which I have for obvious reasons had to curtail very considerably, it is apparent that while the precipitate formed by H_2S in acid tellurous solutions contains the elements in the ratio $Te : S_2$, the quantity of presumably combined sulphur in it varies according to the conditions under which it is produced, and also upon its after-treatment. The quantitative value of H_2S precipitation, in an analytical sense, might, under some circumstances, be turned to useful

* With lithium no doublets have been observed, but a large number of simple lines. If the above law applied to this metal, the interval between its doublets would only be 0·016 (about one-tenth that of sodium). It may be that on account of the want of fineness of most of the lines, this interval is too small for the two components of the doublet to be separated.

account, provided always that the conditions under which operations are carried out are such that the ratio between the constituents of the precipitate is not disturbed, and the latter can be weighed as though it were actually the compound TeS_2. It must, however, be remembered that the precipitate is difficult to manipulate, and, moreover, that its liability to contamination with other substances is in itself an objection to the adoption of the method in any other than most exceptional cases.

(b). Action of H_2S on Alkaline Tellurites.

Berzelius discovered that by passing H_2S through an aqueous solution of K_2TeO_3 for a sufficient length of time, two-thirds of the tellurium present separated as a brown precipitate, which soon became almost black, while the remaining third combined with the K_2S also formed in the reaction and passed into the liquid as potassium thiotellurite: $3K_2TeO_3+9H_2S=3K_2S.TeS_2+2TeS_2+9H_2O$. On filtering off the precipitate and evaporating the filtrate over potash or in a vacuum the thiotellurite is obtained in pale yellow needle-shaped crystals. By substituting $(NH_4)_2TeO_3$ for the potassium salt, the thiotellurite, $3(NH_4)_2S.TeS_2$, is obtained, and its solution on evaporation yields yellow quadratic prisms. Thus, then, if TeS_2 cannot, owing to its instability, be obtained in a separate state, it does exist in combination in these interesting double compounds. A solution of either of the alkaline thiotellurites on exposure to air for a time, or quicker on having a current of air blown through it, deposits a dull grey-black non-crystalline substance which the great chemist believed to be TeS_2, but which I find to be only a mixture of the elements which yields up almost the whole of its sulphur to CS_2. Berzelius observed that the precipitate produced by H_2S in an alkaline tellurite solution, and also that formed by the action of an acid on a solution of an alkaline thiotellurite, had at the moment of its formation a reddish-brown colour, which soon darkened and ultimately became almost black. These changes would indicate the probability of the precipitates so obtained being similar in character to those finally resulting from the action of H_2S on acid tellurous solutions. I did not examine the precipitate formed by decomposing alkaline thiotellurites, but in that produced by H_2S in a solution of K_2TeO_3 I found the ratio of the elements to be $Te : S_2$, and the quantity of insoluble sulphur left behind after extraction with CS_2 to correspond to 6·089 per cent of undecomposed TeS_2. This particular precipitate, however, on boiling for several hours in water containing a little HCl, underwent complete decomposition, the whole of the sulphur in it becoming soluble in CS_2.

(c). Action of H_2S on Telluric Solutions.

Berzelius showed that H_2S is practically without action on dilute solutions of TeO_3 in the cold, but that if saturated with the gas and allowed to remain in a warm place for a sufficient length of time, they first acquire a brown colour without losing transparency, and deposit on the sides of the vessel a black-grey metallic-looking film, which he believed to be the trisulphide, TeS_3. In this connection I made the following experiment:—A telluric solution prepared by dissolving 0·5417 grm. $H_2TeO_4.2H_2O$ in 75 c.c. of water was made up to 350 c.c. with freshly prepared H_2S—water which had previously been acidified with 25 c.c. of sulphuric acid (25 per cent H_2SO_4), and the whole set aside in a closely stoppered flask in a cool dark cupboard for ten days. No appreciable precipitation had taken place at the expiration of that time, but on continuously heating the mixed solution at about 75° for nine days, the whole of the tellurium was thrown down in the condition of a grey-black precipitate, which after drying in CO_2 at 105—110° weighed 0·5295 grm., theory for TeS_3 being 0·5274 grm., and which on extraction with CS_2 left 0·3026 grm., being very little over the calculated tellurium originally present in the $H_2TeO_4.2H_2O$ started with, viz., 0·3000. Thus it is evident that the H_2S precipitate formed in telluric acid solutions does not contain an estimable quantity of combined sulphur, but is composed entirely, or at least nearly so, of an intimate mixture of the elements in the ratio, $Te : S_3$.

(d). The Sulphides of Tellurium.

Tellurium and sulphur can be melted together in all proportions, but it appears that the chemical affinity between the substances ceases at a temperature much below that at which any mixture of them can be fused, and that therefore no definite compound, *i.e.*, sulphide, can be formed in this way.

Some of the results recorded in this paper are necessarily only confirmatory of those obtained by Becker and Brauner, but I have also touched upon several points of interest not dealt with by either chemist, and these I intend to enlarge upon much more fully at some future time, particularly in regard to the thiotellurites and the still less known thiotellurates.

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ON THE

DETERMINATION OF MOISTURE IN HONEY.*

By FRANK T. SHUTT, M.A., F.I.C., F.C.S.,
and
A. T. CHARRON, M.A.

(Concluded from p. 196).

Drying on (a) *Asbestos and* (b) *Sand in Platinum Dishes in Partial Vacuum at 70° C.*

THE apparatus used in these trials was exceedingly simple. A tubulated desiccator was placed inside the steam-bath (the same as used in the foregoing experiment) and connected with an exhaust pump attached to the water service. With a current of dry air at the rate of one bubble per second being drawn through the desiccator, a vacuum of approximately 8 inches was maintained. The temperature of 70° C. was without difficulty kept constant for a week or more at a time by almost filling the bath with water and arranging a series of small gas jets (from an S-burner) at a distance of 3 to 4 inches from the bottom of the bath. The flames were protected from draughts by a casing of asbestos-board.

The absorbent materials were sand and asbestos, and platinum dishes (flat and round bottoms) were used in the place of glass tubes.

TABLE III.—*Moisture in Honey from Fully Capped Comb, as Determined in Partial Vacuum at 70° C.*

Solution A.—60·9166 grms. honey in 500 c.c. (approximately 12 per cent).

Solution B.—25·3596 grms. honey in 500 c.c. (approximately 5 per cent).

Moisture in honey, as calculated for sp. gr. of A = 17·88 per cent.

Moisture in honey, as calculated for sp. gr. of B = 17·46 per cent.

Absorbent material.	Shape of dish.	24 hours.	48 hours.	72 hours.	96 hours.
		From Solution A.			
Sand	F.B.	17·91	18·20	18·67	18·88
	R.B.	17·97	18·24	18·94	19·63
Asbestos	F.B.	20·14	20 83	21 20	21·73
	R.B.	20·16	20 75	21·20	21·98
		From Solution B.			
Sand	F.B.	17·00	17·94	17·94	18·22
	R.B.	16·17	17·12	17·12	17·45
Asbestos	F.B.	22·48	24·89	25·75	26 82
	R.B.	22·83	24·18	25 24	26·15

To compare these results with those obtained by the method previously used, Solutions A and B (using 10 c.c.

* From the *Transactions of the Royal Society of Canada*, vol. viii, p. 35.

in each estimation) were dried at atmospheric pressure in the steam-bath (98° C.) on asbestos in glass tubes, when the following moisture percentages were obtained :—

	24 hours.	48 hours.	72 hours.	96 hours.
Solution A . ..	23·75	26·40	—	—
	24·71	27·12	—	—
Solution B . ..	22·98	30·21	33·92	35·24
	22·20	29·62	32·06	34·05

We now present data of a similar character to those in Table III., but from honey taken from uncapped comb.

TABLE IV.—*Moisture in Honey from Uncapped Comb, as Determined in Partial Vacuum at 70° C.*

Solution.—25·0872 grms. honey in 500 c.c. (approximately 5 per cent).

Moisture in honey, as calculated from sp. gr. = 22·35 per cent.

Absorbent material.	Shape of dish.	24 hours.	48 hours.	72 hours.	96 hours.
Sand	F.B.	21·34	22·65	23·37	23·69
	R.B.	21·52	23·03	23·51	23·99
Asbestos	F.B.	28·45	31·52	33·04	33·32
	R.B.	28·33	31·36	33·04	33·32

The comparative data, drying at 98° C. in steam-bath, using asbestos in glass tubes, are as follows :—

	24 hours.	48 hours.	72 hours.
Percentage of moisture ..	31·34	36·25	40·01
	31·90	36·90	40·53

Drying on (a) *Asbestos and* (b) *Sand in Platinum Dishes in Partial Vacuum at 60° C.*

In all respects, save that of temperature, the conditions of drying were identical with those of the preceding series. The results, given in Table V., appear to show that at this lower temperature (60° C.) twenty-four hours' drying is sufficient for perfect desiccation. As at 70° C., however, the percentages obtained by drying on asbestos are somewhat higher than those when sand is used.

TABLE V.—*Moisture in Honey from Fully Capped Comb, as Determined in Partial Vacuum at 60° C.*

Solution.—59·8312 grms. honey in 500 c.c. (approximately 12 per cent).

Moisture in honey, as calculated from sp. gr. = 17·08 per cent.

Absorbent material.	Shape of dish.	24 hours.	48 hours.	96 hours.
Sand	F.B.	16·88	17·13	17·28
	R.B.	17·62	17·84	18·04
Asbestos	F.B.	18·88	19·24	19·65
	R.B.	18·65	19·20	19·52

The same solution dried on asbestos in glass tubes at 98° C. gave the following results :—

	24 hours.	48 hours.	72 hours.	96 hours.
Percentage of moisture ..	26·27	29·21	30·67	32·26
,, ,, ..	24·66	27·26	28·90	30·33

A review of the results in the foregoing tables allows us to conclude :—

1. That in drying a solution of honey in glass tubes on asbestos, a temperature of 98° C. at atmospheric pressure induces a considerable and continuous dehydration of the levulose, resulting in an apparent loss of moisture far exceeding the real amount present.

2. That drying in glass tubes on asbestos at atmospheric pressure between 70° and 75° C. also occasions a decomposition of the levulose of the honey. It will not suffice, therefore, if accurate results are to be obtained, simply to lower the temperature of the steam-bath as in the second series of experiments.

3. That drying in platinum dishes on sand in a partial vacuum (8 inches) at a temperature of 60—70° C. for twenty-four hours to forty-eight hours, yields results in close accord with those calculated from the specific gravity determinations, and that a more prolonged drying is undesirable, as such appears to induce a slight decomposition of the levulose.

4. That drying on asbestos yields much higher results than drying on sand. This, apparently, is as true at 60° C. as at 70° C. (see Tables IV. and V.), and indicates a peculiar property or quality of the asbestos in inducing decomposition of the levulose.

5. That there were no differences of note between the results from drying in round and flat bottom platinum dishes.

On the Behaviour of Mixtures (Solutions) of Dextrose and Levulose under Varying Conditions of Drying.

As the saccharine matter in honey consists almost entirely of dextrose and levulose, existing in practically equal proportions, it was considered desirable to ascertain the effect of drying solutions of such a mixture, employing methods involving the same conditions of temperature and pressure as in the foregoing tests with honey.

TABLE VI.—*Mixture of Dextrose and Levulose, Drying in Glass Tubes on Asbestos in Steam-bath at Atmospheric Pressure at 98° and 70° C. respectively.*

Dextrose, 5·0009 grms. in 100 c.c.

Levulose, 5·0038 grms. in 100 c.c.

10 c.c. used in each determination = 1·0005 grms.

At 98° C.

48 hours.	60 hours.	80 hours.	93 hours.	120 hours.	132 hours.	140 hours.
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
0·909	0·885	0·864	0·846	0·827	0·818	0·815
0·901	0·877	0·856	0·837	0·817	0·810	0·806

At 70° C.

8 hours.	20 hours.	25 hours.	36 hours.	42 hours.
Grms.	Grm.	Grm.	Grm.	Grm.
1·276	0·954	0·951	0·944	0·943
1·172	0·957	0·956	0·948	0·947

TABLE VII.—*Levulose (Kahlbaum), Drying in Platinum Dishes on Asbestos in Partial Vacuum at 75—80° C. and at 70° C.*

Levulose, 4·465 grms. in 100 c.c.

10 c.c. used in each determination = 0·4465 grm.

Shape of dish.	At 75—80° C. Hours—			At 70° C. Hours—			
	4.	8.	24.	8.	12.	14.	18.
	Grms.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
F.B.	3·236	0·437	0·428	—	—	—	—
	3·153	0·426	0·426	—	—	—	—
R.B.	3·205	0·437	0·424	0·584	0·440	0·437	0·434
	3·746	0·433	0·425	0·479	0·438	0·435	0·431
				0·944	0·443	0·442	0·439

TABLE VIII.—*Levulose (Diabetin, "Schering"), Drying in Platinum Dishes on* (a) *Sand and* (b) *Asbestos in Partial Vacuum at 70—75° C.*

Levulose, 5·472 grms. in 100 c.c.

10 c.c. used in each determination = 0·5472 grm.

Absorbent material.	Shape of dish.	24 hours.	48 hours.
		Grm.	Grm.
Sand	F.B.	0·5385	0·5309
	R.B.	0·5404	0·5290
	R.B.	0·5386	0·5314
Average		0·5392	0·5304
Asbestos	F.B.	0·5293	0·5239
	R.B.	0·5288	0·5206
	R.B.	0·5276	0·5214
Average		0·5286	0·5219

TABLE IX.—*Levulose (Kahlbaum), Drying in Platinum Dishes on* (a) *Sand and* (b) *Asbestos in Partial Vacuum at 60° C.*

Levulose, 5·2228 grms. in 100 c.c.
10 c.c. used in each determination = 0·52228 grm.

Absorbent material.	Shape of dish.	21 hours.	25 hours.	43 hours.	48 hours.
Sand	F.B.	0·543	0·525	0·525	0·525
	R.B.	0·905	0·528	0·528	0·528
Asbestos	F.B.	0·539	0·510	0·510	0·509
	R.B.	0·534	0·507	0·506	0·505

General Deductions from Data in Tables VI. to IX.

The results given in Table VI. show a considerable loss due to decomposition on drying a mixture of dextrose and levulose on asbestos for forty-eight hours at 98° C., and this loss constantly increased. At a temperature of 70° C. (atmospheric pressure), eight hours' drying was insufficient, but an additional period of twelve hours proved too long.

From Table VII. it is apparent that a temperature of 75—80° C. (using asbestos and drying in a partial vacuum) is too high. A drying period of eight hours was sufficient to show that decomposition had commenced. Under the same conditions, but at 70° C., a period of twelve hours furnished results indicating a thorough desiccation of the levulose, but no decomposition. Further drying, however, undoubtedly caused dehydration of the sugar.

In the results of Table VIII. the relative value of sand and asbestos as absorbent materials is compared at 70—75° C. As in the case of honey, we find that with asbestos there is a greater loss on drying than when sand is used. In twenty-four hours the loss through decomposition, using sand, is about 1·4 per cent, whereas with asbestos it is approximately 3·4 per cent. At forty-eight hours these losses, respectively, are practically 3·1 per cent and 4·6 per cent.

The data furnished in Table IX. are indicative that twenty-five hours drying in a partial vacuum at 60° C. on sand is sufficient for desiccation of the levulose, and that there is no decomposition or further loss on continued drying. In the case of asbestos, under the same conditions, there appears to be decomposition (between 2 per cent and 3 per cent) of the levulose. It is evident that even at this low drying temperature sand is the preferable absorbent.

The results of the work on levulose solutions agree very well on the whole with those obtained on solutions of honey. It has already been shown that drying the latter from twenty-four to forty-eight hours at 60—70° C. in a partial vacuum on sand, gave percentages in close accord with those obtained from the specific gravity determinations. The investigations with levulose solutions prove that a temperature of 60° C., in a partial vacuum using sand, furnished figures approximating the amounts weighed out. It is probable that a temperature of 70° C. could be safely used if the pressure were reduced to, say, 6 or 8 inches, but with the partial vacuum that we were able to maintain it is evident that the drying temperature should be as close as possible to 60° C.

School Board for London.—The Annual Exhibition of work from the Day, Evening Continuation, Truant, Industrial, Blind, Deaf, and Physically and Mentally Defective Schools, will be held at the Examination Hall, Victoria Embankment, W.C., on Saturday, May 9th next, from 12 noon till 10 p.m., and on the following Monday, Tuesday, and Wednesday (May 11th, 12th, and 13th), from 10 a.m. till 10 p.m. The Exhibition will be opened at 12 o'clock noon on May 9th by the Right Hon. Lord Reay, G.C.S.I., G.C.I.E., Chairman of the Board. Admission to the Exhibition is free, but tickets are required for the opening ceremony.

THE

TITRIMETRIC ESTIMATION OF NITRIC ACID.*

By I. K PHELPS.

IN the methods for the quantitative estimation of nitric acid which depend upon its reduction with a ferrous salt and the determination of the amount of oxidation produced, scrupulous care is necessary that the atmosphere in contact with the ferrous salt while the nitrogen dioxide is present shall be free from oxygen. This fact was recognised by Fresenius (*Ann.*, cvi., 217; *Zeit. Anal. Chem.*, i., 32), who modified the original process of Pelouze (*Ann. de Chim. Phys.*, [3], xx., 129) by filling the flask with carbon dioxide or hydrogen at the outset. Eder (*Zeit. Anal. Chem.*, xvi., 267) used carbon dioxide similarly. Holland's method (CHEMICAL NEWS, xvii., 219), roughly described, consists in boiling, until the air is expelled, the solution of the nitrate in a flask provided with a doubly bent exit tube, rubber-jointed, and fitted with a pinchcock, then admitting through the tube as the flask cools a mixture of ferrous salt and strong hydrochloric acid, heating the mixture on a water-bath, and, finally, titrating the resulting ferric salt with stannous chloride.

All of these methods give results which are higher than the theoretically expected—those which use carbon dioxide on account of the oxygen invariably present in the gas as ordinarily produced in the laboratory, and Holland's process possibly because of the slow leakage through the rubber connections during the long heating, or because the nitrogen dioxide, which is not driven out completely from the solution of the iron salts, acts somewhat with the atmospheric oxygen during the titration.

Another series of methods has depended upon the determination of the nitrogen dioxide evolved, usually by direct measurement as nitrogen dioxide. Among these may be mentioned the methods of Schloessing (*Ann. de Chim. Phys.*, [3], xl., 479), Reichart (*Zeit. Anal. Chem.*, ix., 26), Schulze and Wulfert (*Zeit. Anal. Chem.*, ix., 400), Tiemann ("Anleitung zur Untersuchung von Wasser," von W. Kubel, Zweit Auflage, von F. Tiemann, 55), Wildt and Scheibe (*Zeit. Anal. Chem*, xxiii., 151), Warington (*Journ. Chem. Soc.*, xxxvii., 468; xli., 345), Boehmer (*Zeit. Anal. Chem.*, xxii., 20), Kratschmer (*Zeit. Anal. Chem.*, xxvi., 608), Wilfarth (*Zeit. Anal. Chem.*, xxvii., 411), Morse and Linn (*Am. Chem. Journ.*, viii., 274), Berger (*Chem. Zeit*, xix., 305), and Roberts (*Am. Journ. Sci.*, 1893, xlvi., 126). In general, these methods give results lower than demanded by the theory—in many cases, on account of the solubility of the nitrogen dioxide in the ferrous solution used as a reducer, and, in other cases, on account of the solubility of that gas in the solution of sodium hydroxide over which it is measured. Further, there is the effect of oxygen upon the nitrogen dioxide; if present in the measuring burette in the proportions found in air, it will not give any appreciable effect in moderate amounts, as was observed by Roberts; but if it is present while the gas is in contact with the ferrous solution, the nitrous or nitric acid formed will be taken up by the solution, and, should the oxygen be introduced continuously, as an impurity in carbon dioxide furnished by a Kipp generator, the iron salts will never be free from oxidised nitrogen. If, however, the oxygen is present in some other proportion of dilution than that of the air—as, for example, in the proportion in which it dissolves in aqueous solutions—it will produce an error no matter whether it comes in contact with the gases of the ferrous solution or those of the collecting burette; in the example taken, the proportion of oxygen being greater than that in the air, the error produced is one of deficiency. The effect of oxygen has been recognised before. For example, in his process of determining nitrates by re-

* Contribution from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, xiv., p. 440.

ducing them with ferrous salt and hydrochloric acid in an atmosphere of carbon dioxide (furnished by the action of hydrochloric acid on marble), boiling the ferrous solution completely to dryness, collecting the gases over mercury, absorbing the carbon dioxide by sodium hydroxide solution, and the nitrogen dioxide by repeated treatment with a concentrated solution of ferrous salt, Warington found that, when the carbon dioxide was made as free from air as possible by using marble boiled in water, and hydrochloric acid also boiled, and adding a little cuprous chloride to the acid, the results were decidedly better.

The estimation of the amount of oxidation of a ferrous salt may be accomplished with a simpler apparatus than that required when the nitrogen dioxide is measured, and the purpose of this article is to put on record such a method, following most nearly the procedure of Holland. The apparatus used consisted of a 250 c.m.^{3} flask closed with a rubber stopper carrying in two perforations the inlet and exit tubes. A stoppered funnel of 50 c.m.^{3} capacity with its tube constricted at its lower end was used as the inlet tube; and a glass tube of 0·8 c.m. internal diameter, enlarged just above the stopper to a small bulb (to prevent mechanical loss of the solid contents of the flask during the boiling), and bent twice at right angles, served as the exit tube.

The analysis was made as follows:—A solution of ferrous sulphate, mildly acidified with sulphuric acid, was made of about one-fifth normal strength, and standardised against standard decinormal arsenious acid solution by treating portions of it, measured from a burette (and weighed as a check on the burette readings) with an excess of decinormal iodine solution, adding about 3 grms. of Rochelle salt in solution, neutralising with acid potassium carbonate, and adding in succession 15 c.m.^{3} of a saturated solution of acid potassium carbonate, starch paste, and then standard arsenious acid solution to the bleaching of the starch blue, and, finally, titrating to colour with the iodine solution. For the determination of nitric acid, the pure potassium nitrate of commerce was used. In the smaller amounts, the nitrate was taken in a solution of known strength measured from a burette, and in the larger amounts as the dry salt. When the solution of nitrate was used, it was measured into the flask, the stem of the separating funnel being completely filled with water, and the exit tube of the flask reaching to the surface of mercury which was placed in a test-tube to the depth of about 3 c.m. The nitrate solution was then boiled to small volume, an amount of the standardised ferrous sulphate solution known to be in excess introduced into the separating funnel, the exit tube plunged a centimetre or two deep into the mercury (which is readily accomplished by changing the position of the flask on the wire gauze, provided that the gauze is depressed well at the centre, and the flask is set well up on the higher part at the beginning of the operation), and then the flame withdrawn until diminution of pressure sufficient to draw the ferrous solution into the flask is made evident by the rise of the mercury in the exit tube. By applying and withdrawing the flame, and by regulating the rate of inflow of the solution, the ferrous salt may be introduced without admitting air, and the funnel washed carefully with an amount of concentrated hydrochloric acid nearly enough to equal the total volume of the liquid in the flask. After the pressure has been restored in the apparatus by heating the flask, the exit tube is again raised to the surface of the mercury, and the solution in the flask boiled to a volume of 10—15 c.m.^{3}. The excess of acid is then nearly neutralised with sodium carbonate solution, the carbon dioxide evolved assisting in maintaining the pressure in the apparatus, so that the condensed liquid in the test-tube which may contain oxidised nitrogen dioxide is not returned to the iron solution; the flask is cooled, and the ferrous salt remaining determined by iodine as previously described, or by a standard solution of potassium permanganate. In case permanganate is used, the contents of the flask are diluted with 600 c.m.^{3} of water, 2—3 grms. of crystallised manganous chloride (Gooch and Peters, *Am. Journ. Sci.*, 1899, vii., 461), and titrated to colour with potassium permanganate. In the experiments where the dry salt was used, the air was expelled from the apparatus by boiling 10 c.m.^{3} of water to small volume in the flask arranged as previously described, the ferrous sulphate solution introduced, and concentrated by boiling to a volume of about 20 c.m.^{3}, so that the amount of acid used may not be so large; then, the nitrate, dissolved in a small amount of water, was allowed to flow in, and was finally washed in, as before, with an amount of concentrated hydrochloric acid, which approximates in volume that of the liquid contents of the flask.

Experiments numbered I.—VIII., inclusive, of the following table show the results of a series of experiments made as described above.

	KNO_3 taken.	Oxygen value of ferrous salt taken.	Oxygen value of ferrous salt found.	Error on oxygen.
	Grm.	Grm.	Grm.	Grm.
I.	0·0500	0·01823	0·00621	0·00015 +
II.	0 0500	0 01865	0·00681	0·00003 −
III.	0 0500	0 01954	0 00768	0·00000 ±
IV.	0·1000	0 02881	0 00507	0·00001 +
V.	0·1000	0 02822	0·00441	0·00008 +
VI.	0·2500	0 06453	0·00512	0·00009 +
VII.	0·5000	0 13394	0·01524	0·00005 +
VIII.	0·5000	0·12210	0·00340	0·00005 +
IX.	0·0500	0 01720	0·00747	0·00214 −
X.	0 0500	0·01550	0·00389	0·00026 −
XI.	0·0525	0·01550	0·00318	0 00014 −
XII.	0·1000	0·02765	0·00432	0·00040 −

Experiments numbered IX. and X. were made to determine whether the long boiling in the previous experiments is actually necessary; for in the work by Fresenius, as well as that of Eder, directions are given merely to boil the hydrochloric acid solution of the iron salt with the nitrate until the colour of the dark compound of the nitrogen dioxide with the ferrous salt wholly vanishes and is replaced by the clear colour of the ferric salt, which means an active boiling of not longer than five minutes in the experiments recorded in the table. Experiment IX. was made exactly like the similar ones above it in the table, except that the boiling was interrupted after the dark coloured ferrous compound with the nitrogen dioxide was completely broken up; and experiment X. similarly, except that the boiling was continued for five minutes after the complete disappearance of the dark colour. Obviously the period of boiling allowed by Fresenius and Eder is not enough, but since the main error incidental to these processes is an error of excess due to oxygen present, as already stated, it will readily appear how this second error, which is one of deficiency, and hence correcting the first error, may have been overlooked.

Ferrous ammonium sulphate has been recommended by Austin and Chamberlain (*Am. Chem. Journ.*, v., 209), and by Rosa (*Gazz. Chim. Ital.*, xv., 295) as more convenient, stable, and sensitive than the crystalline ferrous sulphate. It would seem possible that nitric acid might act as an oxidising agent on the ammonium salt, and certainly nitrous acid (if it were produced, as might be, as an intermediate product in the reduction of nitric acid to nitrogen dioxide) would act according to the equation, $NH_4Cl + HNO_2 = HCl + 2H_2O + N_2$. Such an action either of the nitric acid or nitrous acid would produce an error of deficiency. Experiments XI. and XII. were made to test this point, being made exactly like those numbered I.—VIII., except that 1 grm. of crystallised ammonium sulphate was added with the ferrous salt. The results show slight but appreciable losses.

The concentration of the hydrochloric acid in this operation does not allow of much diminution under these conditions, where immediate reduction of the nitric acid without any volatilisation is a necessity—a fact which has

been recognised before by Roberts and obviated under the conditions there used.

Thus it would appear—

First. That the method outlined above is capable of yielding very accurate results, affording as it does an easy and complete means of shutting out oxygen from the nitrogen dioxide while that gas is in contact with the ferrous salt.

Second. That prolonging the boiling only until the dark coloured compound of nitrogen dioxide with ferrous salt is broken up, results in the incomplete reduction of the nitric acid.

Third. That ammonium salts must be absent if the highest accuracy is desired.

NOTICES OF BOOKS.

A Text book of Organic Chemistry. By A. F. Holleman. Translated from the Second Dutch Edition by A. Jamieson Walker, assisted by Owen E. Mott. With the Co-operation of the Author. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. xvii.—555 pp., 8vo. Ill. Also issued in two parts; Part I., Introduction and Fatty Compounds. Part II., The Aromatic Compounds and Substances related to them.

This forms a companion volume to the author's "Text-book of Inorganic Chemistry," translated by Hermon C. Cooper, and published by the same firms in 1902; and in it the same high plane is maintained. Dr. Holleman has endeavoured to keep the number of unconnected facts within as narrow limits as possible, to avoid confusing the beginner, and he has given prominence to underlying theories. For most of the compounds proof of their structure is given, but the methods of orientation employed for the higher substitution products of the aromatic series are described in a separate chapter. Features of this comprehensive text-book named in connection with the notice of the first volume are introduced into the second wherever the nature of the subject permits; prominence is given to the modern physico-chemical theories, such as the laws of equilibrium, ionisation, &c. Some of the more important technical processes are briefly discussed.

Structural, displayed formulæ are freely used, and the text explaining the reasons for so representing the bodies is unusually clear; at several points stereo-isomerism receives due attention. Space is found to notice some unusual compounds, such as the tertiary bismuthines, Grignard's magnesium alkyls, and certain esters, yet the author disclaims any attempt to make the book a "Beilstein."

The contents of the volume are set forth in an unusually full table occupying nine pages, and there is also an ample index of twenty-seven pages, facilitating reference.

To point out more admirable features would make this notice read like a table of contents, and we conclude by strongly recommending this thoughtful philosophical text-book. Both volumes are well clothed, as usual with these publishers; and taking bulk, as well as quality, into consideration, the price is low. H.C.B.

A Short Manual of Inorganic Chemistry. By A. Dupré, Ph.D., F.R.S., &c., and H. Wilson Hake, Ph.D., F.I.C., &c. Third Edition (re-issue). London: Charles Griffin and Co., Ltd. 1903. Pp. 391.

In a publisher's note we read that the opportunity has been taken of the re-issue of this popular work to meet an urgent request of many teachers for a less expensive edition. The present edition, while retaining the main features of the preceding editions, has been thoroughly revised and partly re-written, with special reference to the periodic law, and has thus undergone some material alterations.

The growing importance of physical chemistry, and especially of thermo-chemistry, has necessitated considerable alterations and additions to the introductory portion of the book. In the descriptive part, which commences on page 102, the authors have adhered to the arrangement outlined in their "Scheme of Properties," but they have adopted the periodic system of classification, and have taken the elements in the order of grouping according to Mendeleeff's table, which is given on page 98. The book is well written, and the descriptions are clear and ample. There is a short appendix containing a few useful tables, and a very full index of thirteen pages of two columns each.

Logarithmic Tables for Chemists ("Logarithmische Rechentafeln für Chemiker"). By Dr. F. W. Kluster. Third Edition, Revised and Englarged. Leipsic: Veit and Co. 1902. Pp. 93.

Besides a useful table of five-figure logarithms from 100 to 9999, and a supplementary one from 10 to 99, the author has given a number of other tables which will be of great convenience to those who have many calculations to make on chemical matters. Among these other tables we may mention those of the atomic weights of all the elements, and their logarithms, factors and their logarithms for finding the weight of any element from various salts, the molecular weights of a large number of salts and their logarithms, and similar tables for use in the volumetric estimation of gases, &c.; the whole collection being bound in a convenient form.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 22.

The Acid Reaction of the Alums, and the Influence of this Acidity on the Insolubilisation of Gelatin in the case of Chrome-alum.—MM Lumière and Seyewitz. —The authors have examined the cause by which the alums may be treated with a considerable amount of alkali without the precipitation of the oxides, and they have determined, in the case of each alum, what quantity of alkali corresponds to the persistent precipitation of the oxide. They have also examined the difference between the insolubilisation by means of neutralised chrome-alum, and the same unneutralised, with a view to determining the best conditions to obtain the most complete insolubilisation, and they found that the best results were obtained by treating the alum with an alkali until a slight persistent precipitate was formed.

Estimation of Sulphurous Acid by means of a Titrated Iodine Solution.—A. Berg.—Already inserted in full.

Synthesis of the Ketones and Acylacetones starting from the C-acylacetic Ethers.—E. Bouveault and A. Bongert.—When a C-acylacetic ether is heated with concentrated hydrochloric acid to 130—140° in a sealed tube, we obtain carbonic acid, alcohol, acetic acid, and a ketone, according to the equation—

$$CH_3—CO—CH(CO—R)—CO_2R' + 2H_2O =$$
$$= CH_3—CO_2H + CH_3—CO—R + CO_2 + R'OH.$$

The reaction is quasi-integral; the authors have applied it, in particular, to C-butyrylacetylacetate of methyl,

which gave methylpropylketone, recognised by its odour and its boiling-point. When a C-acylactylacetic ether is heated with water to 140—150°, in a sealed tube, an acylacetone is formed, as well as carbonic acid, and the alcohol corresponding to the ether originally used. Experiments show that the acylacetones have most of the characteristic properties of acetylacetone.

Synthesis of Acylacetic Ethers by means of the C-acylacetylacetic Ethers. — L. Bouveault and A. Bongert.—An excess of boiling dilute potash decomposes the C-acylacetylacetic ethers according to the equation—

$$CH_3—CO—CH(CO—R)—CO_2R' + 3KOH = CH_3—CO_2K + CH_3(CO—R) + CO_3K_2 + R'OH.$$

The authors thought that by conducting this reaction more carefully they might be able to obtain a product of an intermediate decomposition. They have studied this reaction in detail on C-butyrylacetylacetate of methyl, and describe a number of products obtained.

Reactions and Decompositions of C-acylacetylacetates.—L. Bouveault and Bongert.—In this paper the authors give the results obtained from their experiments on the reactions of the C-acylacetylacetates with hydrazine and phenylhydrazine; for this purpose they used the butyrylacetylacetate of methyl.

Action of the Chlorides of the Acids on the Soda-derivatives of the Substituted Acetylacetic Ethers.—L. Bouveault and A. Bongert.—If the sodium salt of butyrylacetylacetate of methyl is treated with iodide of methyl, either in the dry state or in ethereal solution, no reaction takes place; but if we add alcohol, or what comes to the same thing, if we add iodide of methyl to the mixture of C-butyrylacetylacetate of methyl and methylate of sodium, after a few minutes a slight heating takes place; this increases until the boiling-point is reached if the solution is not sufficiently dilute. After standing a few hours, the alcohol and the iodide of methyl are driven off on the water-bath *in vacuo* until the precipitation of the iodide of sodium puts a stop to the distillation; the product is poured into water, and an oily layer is formed immediately, which is extracted with ether. This ether is driven off on the water-bath, and the product re-distilled *in vacuo*. As the reaction took place in a manner which appeared to be entirely normal, the authors expected to obtain the methylbutyrylacetylacetate of methyl, a liquid boiling at about 110° at 10 m.m.; but they were astonished to find a colourless liquid with an agreeable odour boiling at only 89—90° at 16 m.m., of density at 0° and 4 m.m. = 1·005. Analysis gave figures corresponding with the formula $C_8H_{14}O_3$. Thus the expected body was decomposed at the moment of its formation, losing an acetyl group; in fact, the compound $C_8H_{14}O_3$ constitutes methylbutyrylacetate of methyl. The authors subjected this new body to an extended examination, and amongst other experiments they combined it with phenylhydrazine and with hydrazine.

Some Derivatives of Azobenzene and of Hydrazobenzene.—P. Freundler and L. Beranger.—This research, of which the results are given in this paper, was undertaken with the object of preparing the alcohols, aldehydes, ketones, and the acid derivatives of azobenzene. These compounds, which have the general formula $C_6H_5—N=N—C_6H_4—R(R=CH_2OH,CHO)$, &c., have a certain interest from the point of view of their odour. The authors then describe three methods by which the dissymmetric derivatives of azobenzene may be obtained.

Examination of Essence of Vervein from Grasse.—Eug. Theulier.—The essence examined was obtained by the distillation of the fresh leaves of the *Verbena triphylla, L.*, from the neighbourhood of Grasse; 180 kilos. of leaves gave 130 grms. of essence, or 0·72 per cent. After filtration the essence obtained had the following properties:—

Density at 13°	1·919
Rotatory power	−16° 20′
Ethers, as acetate of linalyl	11·20 per cent

It is insoluble in alcohol at 80°, but soluble in its own volume of alcohol at 90°; on the addition of a further quantity of alcohol it does not become cloudy, but small, white, very brilliant flakes separate out. When the ethers are estimated, the solution of alcoholic potash immediately causes a bright red colouration. This essence contains only a small proportion of aldehydes (20 80 per cent), but it is characterised by the presence of a stearoptene fusing at 62·5°, and easily separated on cooling. It contains, besides citral, levogyre limonene, geraniol, and a sesquiterpene.

Methylanthranilate of Methyl in the Vegetable Organism.—Eugene Charabot.—Already noticed.

The Use of Animal Charcoal in the Analysis of Wines; its Advantages and Disadvantages. — M. Carimantrand.—Not suitable for abstraction.

A New Apparatus for the Estimation of Nitrogen.—Ch. Porcher and M. Brissac.—Requires the accompanying diagram.

The Nature of Bufonine.— G. Bertrand.—The author is of the opinion that Faust's bufonine is not a new principle; it is simply ordinary levogyre cholesterine contaminated by various impurities, among which a small amount of bufotaline gives it a certain activity on the heart of a frog.

MISCELLANEOUS.

The Existence of the Blue or Green Modification of Sulphur.—N. A. Orlaf.—In a previous paper the author has described the formation of blue or green sulphur by the action of S_2Cl_2 on certain metallic sulphides in the presence of organic solvents. The colouration of the sulphur thus produced is not due to organic mixtures; this has been proved by analysis, and also by the fact that the presence of the organic solvent is not indispensable. Neither is it due to the presence of polysulphurised or chlorosulphurised compounds, for the coloured sulphur has no action on sulphuretted hydrogen, and its transformation by means of alcohol gives a white material, and not a black (Bi_2S_3) or yellow (CdS) one. The author describes various reactions which give rise to the formation of green or blue sulphur; the conclusions to be drawn from his experiments may be summarised as follows:—1. A large number of facts tend to prove that a blue or green (caused by mixing with the yellow sulphur) modification of sulphur does exist, but it is very unstable, and can only exist under certain special conditions, such as fixation on the metallic chlorides at the moment of its separation from certain compounds, the presence of certain mineral or organic compounds. 2. Among the conditions favourable to the formation of blue sulphur, we must note particularly the phenomena of apparent dissociation and the reactions which remain incomplete; the reaction of Caraves Gil, which consists of pouring a few drops of a solution of a polysulphide of Na, K, NH_4, or Ca into concentrated boiling alcohol; a blue or bluish-green colouration is formed, which disappears on the addition of an alkali or of any other substance capable of decomposing the polysulphide; the alcohol may be replaced by acetone. In this connection we may mention the experiments of Nöllner (decomposition of KCNS alone, or in the presence of KOH), and of Geutner (action of heat on a solution of SO_2 in sealed tubes in the presence of $BaCO_3$, $SrCO_3$, &c.) as giving blue sulphur. 3. The structure of blue sulphur is uncertain, but in any case the reaction of CdS on S_2Cl_2, the experiments of Geutner, and even the

colour of the product, would point to a structure similar to that of ozone (S_3). The preparation of blue sulphur in a pure state offers difficulties as great as the preparation of pure ozone. Although the blue sulphur may be very unstable in the free state, it may form a very stable chromophore group when fixed with certain substances. The author thinks that we might look upon sulphur as the chromophore of certain mineral colours, particularly of ultramarine.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 52.

The Hydrates of Calcium Oxide.—F. F. Sélivanof.—The author has succeeded in strongly concentrating a solution of $Ca(OH)_2$ in water by congelation. He obtained a new crystallised hydrate, $Ca(OH)_2.H_2O$; these crystals have a very strong double refraction; they do not contain any CO_2. The author has examined the solubility of $Ca(OH)_2$ in dilute solutions of sugar, and finds that amorphous $Ca(OH)_2$ is more soluble than crystallised $Ca(OH)_2$.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., Part 2, p. 14.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Society of Arts, 8. (Cantor Lectures). "Mechanical Road Carriages," by W. Worby Beaumont, Mem.Inst.C.E.
—— Society of Chemical Industry, 8. "Problems in the Fat Industry," by Dr. Julius Lewkowitsch. F.I.C.
—— Royal Institution, 5. General Monthly Meeting.

TUESDAY, 5th.—Royal Institution, 5. "The Blood and some of its Problems," by Prof. Allan Macfadyen, M.D., &c.
—— Society of Arts, 4.30. "The Lagos Hinterland—its People and its Products," by Major J. H. Ewart.

WEDNESDAY, 6th.—Society of Arts, 8. "The Construction of Maps and Charts," by G. J. Morrison.
—— Society of Public Analysts, 8. "Existing Defects and Possible Improvements in the Laws relating to Adulteration," by Alfred H. Allen, F.I.C. "The Composition of Milk," by H. Droop Richmond, F.I.C.

THURSDAY, 7th.—Royal Institution, 5. "Hydrogen — Gaseous, Liquid, and Solid," by Prof. Dewar, F.R.S., &c.
—— Chemical, 8. "β-Bromonitrocamphor and β-Bromocamphoryloxime—Influence of Impurities in Conditioning Dynamic Isomerism" and "Spontaneous Decomposition of Nitrocamphor," by T. M. Lowry. "The Active Constituents of *Butea frondosa*," by E. G. Hill.

FRIDAY, 8th.—Royal Institution, 9. "Rural England," by H. Rider Haggard.
—— Physical, 5. "A Spectroscope of Direct Vision and Minimum Deviation," by T. H. Blakesley. "Mathematics of Bees' Cells," by Prof. Everett. "The Coloured Map Problem," by W. H. Price. "Note on the Construction and Attachment of Galvanometer Mirrors," by Dr. W. Watson.

SATURDAY, 9th.—Royal Institution, 3. "Music" (with Musical Illustrations), by Hamish MacCunn.

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THE CHEMICAL NEWS.

VOL. LXXXVII., No. 2267.

CAMBRIDGE CEMENT-STONES.

By EDWY G. CLAYTON, F.I.C., F.C.S.

DURING recent years the hydraulic cement industry has been largely carried on in the valley of the river Rhee or Cam, a short distance south-west of Cambridge. The names of the places marking the direction of that part of the valley are Trumpington, Hauxton, Haslingfield, Harston, Barrington, Foxton, Shepreth, and Meldreth. Several cement works are situated in this district, and the products are claimed to be equal to Portland cement from the Thames and Medway. The river flows through Upper Cretaceous strata; the chalk marl and lower chalk being well developed on the right bank, the gault on the left, and along the course of the stream is a tract of alluvium of varying width.

The results of analyses of some specimens of cement-marl, &c., from the neighbourhood are given in the accompanying table.

Sample	Cement-marl. 1.	2.	3.	4.	5.	6.	7.	8.	Grey chalk.	Boulder clay from the district.
Silica	18·15	23·39	25·20	21·75	22·00	13·75	14·67	16·43	5·48	47·58
Calcium carbonate (*a*)	70·15	65·44	67·57	70·80	71·16	79·30	79·27	75·92	87·94	36·51
Iron oxide and alumina	5·72	3·05	3·82	2·71	3·44	2·11	2·05	2·42	1·20	10·12
Magnesia, alkalis, &c.	2·74	5·31	0·17	0·73	0·67	1·72	0·43	2·04	4·81	3·55
Loss at 100°	3·24	2·81	3·24	4·01	2·73	3·12	3·58	3·19	0·57	2·24
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

(*a*) Equals an average of 74·88 per cent on the samples of marl, dried at 100° C.

Chemical Laboratory,
32, Holborn Viaduct, London, E.C.,
April 28, 1903.

SLIPSHOD METHODS OF OIL AND PAINT ANALYSIS, AND THE TWENTIETH CENTURY NEGLECT OF INORGANIC CHEMISTRY.

By JOHN GEDDES McINTOSH.

WITH the exception of the chemistry of the rare metals, the present-day neglect of inorganic chemistry is very palpable and much to be regretted. Prof. Reynolds' suggestion (in his Address summarised in the CHEMICAL NEWS, vol. lxxxvii., p. 188) that inorganic chemistry should receive more attention is highly opportune. If evidence of this were required it is to be found in the slipshod methods of inorganic analysis given in most books dealing with the technology of substances which fall within the domain of organic chemistry. Take the determination of the inorganic substances dissolved in oils either for increasing their lubricating or drying propensities. Two of the most important ingredients are lime and lead compounds. Lime is detected and estimated without removing lead, and lead is estimated without separation from lime, and so on. One would think the authors of the text-books in question had never gone through the group separations in their life, and yet these men are looked up to as authorities, and are the parents of organic substances the formulæ for which would almost require a folio page of the "Encyclopædia Britannica" to thoroughly display. But the pity of it all is that the ordinary layman is apt to attribute no value whatever to formulæ which owe their parentage to so-called authorities who by their writings show that they are ignorant of the mere rudiments of inorganic analysis. It is, in fact, only too highly probable that their organic separations are as faulty as their inorganic ones. The same is the case with most of the schemes for the analyses of mixed paints; lead is again prescribed to be estimated without separation from lime, and so on.

Take the text-books on oils again. Page after page are taken up with the so-called constants of oils—the data given being of no value whatever except in regard to the particular sample operated on. But they have the mischievous effect of confusing those who consult such treatises in the search for information. Then, to show how far these so-called authorities appreciate and understand the results of those in the field before them, Allen's figures, as given in his "Commercial Organic Analysis," are quoted as if they were the results of a series of analyses made by Allen personally. I was always under the impression that these figures were the *maxima* and *minima* of the results obtained by all and sundry up to the publication of Allen's book, but that it did not necessarily follow that Allen had made *all* these determinations personally.

It almost looks as if the compilers of these so-called "constants" took a savage delight in piling up elaborately designed tables for the express purpose of confusing the reader, and that the more he succeeded in doing so, the more he gloated over his handiwork. It is high time that these "constants" were "wiped off the slate," and something *less variable* put in their place. No two animal or vegetable oils of the same nature are absolutely identical, but it is giving the student of oils altogether an erroneous idea to lead him to the belief that they vary within the highly wide range of the piles of so-called constants. If they vary there is a cause for it, and efforts should rather be made to discover the cause of the variation than to register the results in the hope of their being added to the already enormously swollen tables of results of no value except in regard to the individual samples of oil to which they refer. Again, the term "value," as used in "saponification value," &c., is not a very intelligible one. It may be the literal meaning of the German *Zahl*, but it has not got the meaning in English which it is intended to convey in the technical sense in which it is used. Not only so, but far from affording a complete means of *valuing* an oil, it is merely an *indication*, and taken by itself in many cases an unreliable *indication* at the best. Again, prefixing a man's name in front of "value" makes it still more ridiculous; and, as if this were not enough, in the case of the so-called "Reichert value" we must needs express an acid determination in terms of c.c. of decinormal potash! The absurdity of this latter method of expression was recently animadverted on by two French Government Agricultural Chemists. The nomenclature of oil analysis, or the words in which the results are expressed, are sadly in want of revision.

9, Parsonage Street, Cubitt Town, E.

THE STRUCTURE OF SPECTRA.*

By Prof. CH. FABRY.

(Continued from p. 209).

III. *The Series.*

The groups present in a spectrum are not isolated one from the other, they are arranged in natural families which we will call series.

The first example of a series of lines was discovered in the hydrogen spectrum. Fig. 1 shows this spectrum on the scale of frequencies, as found by Cornu's measurements; the intensity of the different lines is indicated roughly by the thickness of the marks.

Since then, Messrs. Hale and Deslandres have discovered, in the spectra of solar protuberances and of certain stars, 16 other lines belonging to the same series, which brings the total number up to 28, all of which are represented very accurately by Balmer's formula.

The spectra of the metals show series entirely analogous to those of hydrogen; instead of simple lines, the elements of these series will be the doublets or triplets of which we have already spoken, and a single metal will give several distinct series, related to each other by very simple laws. As these series confuse each other, most careful observations have been necessary to separate them, while in the case of hydrogen it was sufficient, as shown by Cornu, to free the spectrum of all strange lines to see the series unique in all its simplicity.

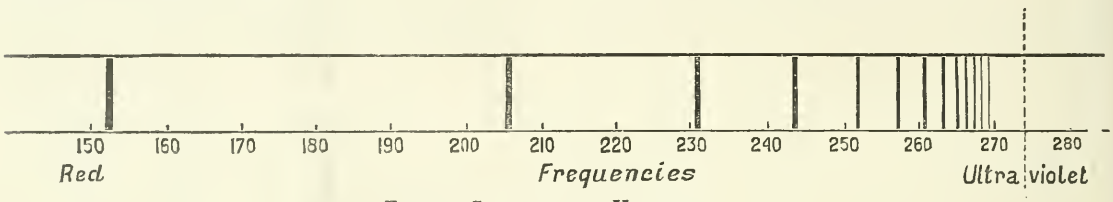


FIG. 1.—SPECTRUM OF HYDROGEN.

A simple glance suffices to show that these lines are not placed haphazard. Their intensities diminish regularly at the same time as the wave-lengths, as well as the distance from each line to the next. They seem to tend towards a limit which would correspond to the frequency 274, or to the wave-length 364·6 $\mu\mu$. To show this regular distribution more precisely, let us project this spectrum on a graphic curve; the lines must be numbered from 3 to 15, and for each line we will plot the numbers of the order m as abscissæ, and the frequencies N as ordinates. We see in Fig. 2 that the points form a

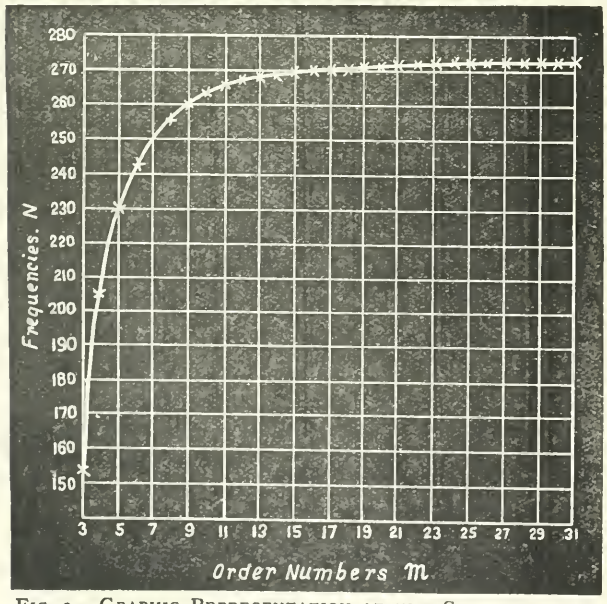


FIG. 2.—GRAPHIC REPRESENTATION OF THE SPECTRUM OF HYDROGEN.

perfectly regular curve which has a horizontal asymptote.

In 1885 Balmer showed that this curve is represented *exactly* by the equation—

$$N = \frac{B}{4} - \frac{B}{m_2},$$

B being a constant.

Let us take as an example the spectrum of potassium, in which we have already discovered doublets having a constant interval, which we will call v.

The close examination of this spectrum shows that its lines are divided by their simple appearance into three categories:—

1. Very brilliant lines which appear even when the metallic vapour is not at a very high temperature, as in a Bunsen flame. They are easily reversible; we will call them the principal series.

The other lines only appear at the highest temperature, in the spectrum of an electric arc charged with potassium vapour, for example.

Here we distinguish:—

2. Fairly wide lines, but with indistinct edges, especially at the red end; they form what Rydberg calls the diffuse series, and Kayser and Runge the first secondary series.

3. Narrow lines of symmetrical appearance, less brilliant than the preceding ones; they form the narrow series, or the second secondary series.

Fig. 3 shows these three series separately; their superposition represents the complete spectrum of potassium, very confused as we know.

In both series the intensities decrease as we approach the ultra-violet; and each series is analogous in its appearance to the series in the hydrogen spectrum.

Let us examine first one of these secondary series; the first, for example. It is formed of doublets all having the constant interval, v. Therefore it is sufficient to consider one line only of each pair. By representing the frequencies of these lines by plotting analogous to that done for hydrogen, we obtain a curve of the same form with a horizontal asymptote corresponding to the limit of the series (Fig. 4, curve s_1).

This curve is not only analogous to that of hydrogen, but it is almost exactly superposable by two displacements parallel to the axes of the co-ordinates. Thus we can represent it by an equation of the form—

$$N = A - \frac{B}{(m+\mu)_2}.$$

A, B, and μ are constants, and B has practically the same value as in Balmer's formula. This generalisation of Balmer's formula is due to Rydberg.

If we had taken the second component of each pair of lines we should evidently have found the same curve, dis

* *Revue Générale des Sciences*, Year XIV., No. 5, March 15, 1903.

placed vertically by the amount v; the constant A would simply be changed to $A+v$. This curve has not been placed in the figure, in order to avoid too great complications. It is deduced from s_1 by an upward displacement of 0·3 m.m.

The second secondary series is also formed of doublets with the constant interval v. It again will be represented by two curves, of which one is the curve s_2 in Fig. 4. We pass from the two curves of the first series to those of the second series by a simple horizontal displacement. The asymptotes are not changed. *The two secondary series have the same limits.*

Finally, we come to the principal series. It is composed of doublets, but only the first of these has the interval v. The others become more and more narrow as we advance towards the small wave-lengths, and their interval tends towards zero.* By using once more the same method of graphic representation, we shall get two more curves. These two curves are superposable by a simple horizontal movement; they have the same asymptote, which means also that the interval of the doublets tends towards zero. We have only shown one of these curves in Fig. 4 (curve P). The other can be made by a simple horizontal displacement of 0·02 m.m. These two curves of the principal series are again almost superposable on those representing the secondary series.

We can see that a single curve displaced successively by suitable amounts in both directions represents the whole of the three series of doublets. Still this superposition of curves is not perfectly exact; while in the case of hydrogen Balmer's formula seems to be absolute, in the case of the metals that of Rydberg is only approximate. Kayser and Runge have given more exact formulæ with a larger number of constants. These are but empirical formulæ. Still the very closely approximate representation of all the series by one single curve is none the less very remarkable.

The other alkaline metals give entirely analogous results, and it is very interesting to compare these spectra with each other. We have already seen that the constant v increases as the square of the atomic weight. If we compare the *limits* of the different series, we find that they approach the red as the atomic weights increase. This is true both for the limit of the principal series and for the limit of the secondary series, as shown by Fig. 5.

Thus we find confirmed what was announced more than twenty-five years ago by M. Lecoq de Boisbaudran, that the spectra are displaced towards the red end as the atomic weights increase, as if the greater mass of the atoms caused their movements to be slower.

Other natural families of metals also have regular and analogous spectra; their structure is similar to that of the spectra of the alkaline metals, but the principal series is at fault, or at least it is no longer represented except by a single known element. The doublets are replaced by triplets in the case of the divalent metals. Thus we have only two series formed of identical groups (doublets or triplets), which is indeed the character of the secondary series. As for the alkaline metals, the limits of these two series are the same. In one natural family of metals

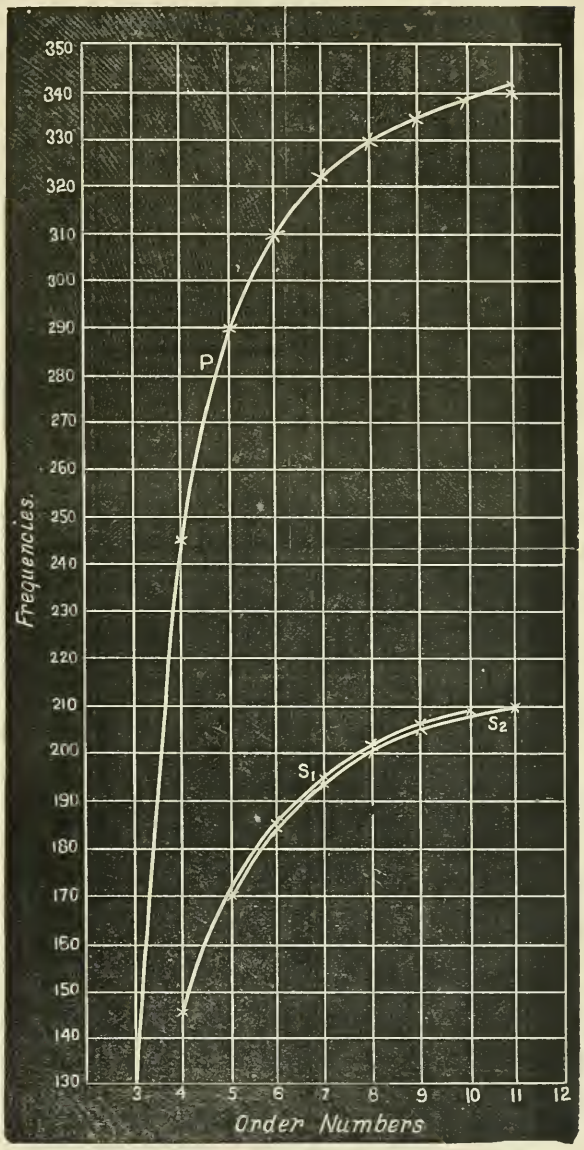


FIG. 4.—GRAPHIC REPRESENTATION OF THE SPECTRUM OF POTASSIUM.

these limits move towards the red end as the atomic weights increase, and at the same time the doublets or triplets become wider.

The representation of all these series by a single form

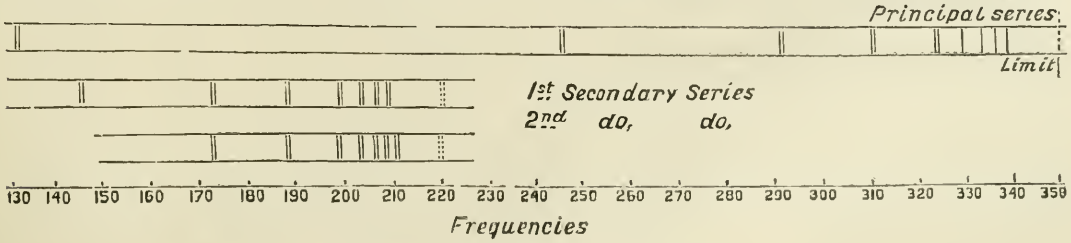


FIG. 3.—SPECTRUM OF POTASSIUM.

* In Fig. 3, we have only been able to show the first doublet of the principal series as a double line. For the others, the two components become confused on the scale to which the drawing is made.

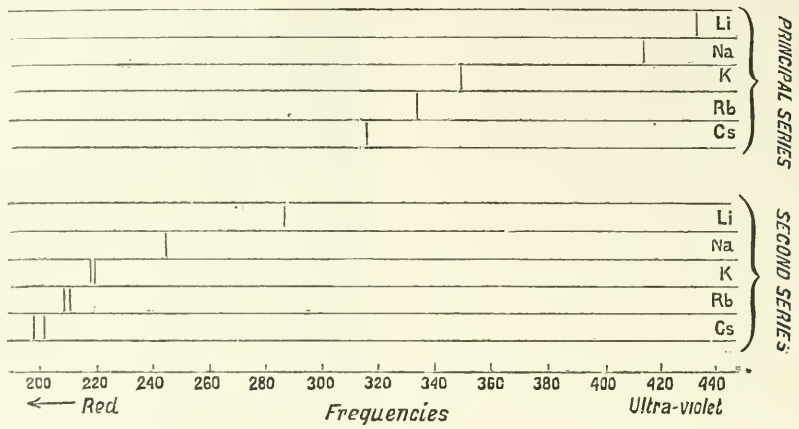


Fig. 5.—Limits of the Series of Alkaline Metals.

of curve, more or less displaced parallel to the axes of the coordinates, is one of the most remarkable facts. If we put on one side the position of this curve, and deal only with its shape, which alone remains practically invariable, we observe that it is characterised by the single constant B. It is difficult to get rid of the idea that we have here one of the important constants of nature, since, in spite of slight variations, it characterises not only the properties of a body or of a natural family of bodies, but also those of very diverse simple bodies. It appears to represent a property of matter, of which the simple significance escapes us for the present.

(To be continued).

SOME CELLULOSIC CONSTITUENTS OF ORANGE-PEEL.

By H. STANLEY.

Cross and Bevan ("Cellulose," p. 236, 1895 ed.) say:—"The cellular tissue of the plant being regarded as the seat of essential vital operations, . . . whereas the cuticular tissues are mainly concerned in closing off and protecting the tissues beneath from the unregulated action of water and air." And again:—"They (the tissues) are largely depleted of organic nitrogenous matter, upon which vitality depends, and have ceased to live in the full sense of the term, but, on the other hand, are known by casual observation to live in the sense opposed to decay." The "death" is accompanied by condensation processes, with increase of carbon percentage at expense of oxygen and hydrogen.

The results of elementary analysis of the peel are given below. For this purpose the peel was divided into its two main layers; the outer one of the typical orange colour, and the inner one white and of softer texture.

(*Note.*—Unless otherwise stated, the whole thickness of the peel is to be understood, and in all cases dried at 100–105° C.).

Inner Layer.—0·1649 grm. gave 0·2945 grm. CO_2, 0·0860 grm. H_2O, and left 0·0047 grm. white ash. Hence (ash free), C = 50·44 per cent, H = 5·96 per cent, O = 43·60 per cent. The peel contains no nitrogen. The ash preserves to some extent the skeleton of the original fragments, and amounts to 2·95 per cent. The above composition corresponds closely to the formula $C_{34}H_{48}O_{22}$, which, curiously enough, is given to oak wood by W. A. Miller on the results of a similar analysis.

Outer Layer.—The results may here be vitiated by the presence of traces of essential oils not removed by drying. It was expected that this layer would have had the higher carbon percentage, which, however, is not apparently the case. 0·1648 grm. gave 0·2703 grm. CO_2, 0·0946 grm. H_2O, and left 0·0046 grm. white ash. Hence (ash free), C = 45·78 per cent, H = 6·37 per cent, O = 47·85 per cent, ash = 2·84 per cent. The proportion of carbon is in both cases higher than that required by the formula $C_6H_{10}O_5$ (C = 44·2, H = 6·3, O = 49·5).

Action of Acids.

Hydrochloric Acid.—This speedily causes blackening and disintegration, even at a moderate temperature and dilute (1·06 sp. gr.); on distillation furfural is obtained. The general method of Tollens for detection of hexa-carbohydrates by the production of levulinic acid was tried, but with negative results; the products of the reaction either after prolonged exposure to acid of 1·1 sp. gr. or on boiling, gave no colouration with the resorcinol reagent.

Sulphuric Acid.—The action here takes an entirely different course. On boiling the peel with the dilute acid, it is very slowly disintegrated, and a brown solution is obtained. On cooling, a slight flocculent precipitate appeared, the quantity of which was increased by addition of alcohol, and still further increased in alkaline solution. On addition of alkali (NaOH), a marked deepening in the colour of the solution takes place, and the gelatinous precipitate is orange coloured, whereas in acid solution it is colourless. The reaction was examined quantitatively, with regard to cupric reducing power, by the use of Fehling's solution. The results are given as per cent of glucose on the original weight of the dried peel.

Time of boiling.	Weight of peel. Grms.	Amount of acid. C.c.	Strength of acid. Per cent.	Glucose. Per cent.
Five minutes	2	30	6·5	14·8
Fifteen minutes	2	30	6·5	17·2
Fifteen minutes	2	60	3·2	19 3
Fifteen minutes	3	80	3·2	20·1
Thirty minutes	8	400	2·0	23·7
Fifteen hours (ordinary temperature)	2	30	6·5	12·9
Fifteen hours (ordinary temperature)	5	100	13·0	20·0

The limit approximates to 20 per cent. The solutions obtained were without action on polarised light both before and after removal of the gelatinous precipitates The latter appeared at first to be of the nature of dextrin, but the following characteristics point to a different conclusion:—They are slightly soluble in water; their solutions are optically inactive and give no colouration with

iodine; they do not unite with phenylhydrazine (acetate), and do not reduce Fehling's solution. All attempts to crystallise out a sugar from the products of hydrolysis failed, but a slight yield of an osazone (?) was obtained, m. p. 161—162°.

Nitric Acid.—The dilute acid (1·14 sp. gr.), by prolonged action at ordinary temperatures, produces slight disintegration; the peel becomes almost colourless and the solution deep brown, whilst a yellow gelatinous precipitate, similar to the one mentioned above, separates out. The solution was filtered from undissolved matter, and the filtrate examined qualitatively; no mucic acid and but traces of saccharic acid were present, but oxalic acid appeared in some quantity. Hexoses are therefore not present in appreciable amount.

Furfural Estimation.

The dried peel was distilled with HCl (1·06 sp. gr.) and the furfural collected and weighed as hydrazone in the usual manner. The first few cubic centimetres of distillate contained a small amount of a yellow oil, which was separated.

5 grms. gave 0·681 grm. hydrazone = 7·3 per cent.
4 " " 0·528 " " = 7·1 per cent.

The inner and outer layers were examined separately; the yellow oil being found to come exclusively from the outer layer.

4 grms. inner layer gave 0·580 grm. hydrazone = 7·8 per cent.
4 grms. outer layer gave 0·575 grm. hydrazone = 6·9 per cent.

An orange which had been kept for (at least) thirty years, and allowed to shrivel up, and which weighed but 14 grms. (about one-tenth of its original weight, probably), was broken up, and gave the following numbers:—

3 grms. gave 0·450 grm. hydrazone = 8·0 per cent.
3 " " 0·455 " " = 8·1 "

Here an increase of about 0·8 per cent is noted, and points to slightly increased lignification (not necessarily so, however, as the furfural in some cases decreases with age).

Cellulose Estimation.

Chlorination Method (*Cross and Bevan*).—The peel was boiled with alkali and exposed to chlorine, followed by treatment with dilute sodium sulphite; the addition of the latter caused a not very marked red colouration, which disappeared on boiling. The almost white residue was washed with sulphurous acid, and finally with water, dried, and weighed.

5 grms. (1 per cent soda, fifteen minutes) gave 1·10 grms. residue = 22·0 per cent.
5 grms. (1 per cent soda, thirty minutes) gave 1·02 grms. residue = 20·4 per cent.

Nitric Acid Method.—The loss caused by the action of the dilute acid is considerably less than that caused by the chlorination process (preceded by alkaline treatment). The reverse is usually the case with compound celluloses, the acid attacking both the ligno-cellulose and the less resistant or β-variety of cellulose.

5 grms., heated at 60—70° with acid (1·14 sp. gr.), washed, and dried, gave a residue preserving to some extent the form of the original, and of a pale yellow colour, and amounted to 2·74 grms. = 54·8 per cent.
5 grms. at 60—80°, for a longer period, gave 2·42 grms. residue = 48·4 per cent.
Schulze's Process.—4 grms., treated with 100 c.c. HNO_3 (1·10 sp. gr.) containing 0·3 grm. potassium chlorate for six days at ordinary temperatures, gave 2·33 grms. residue = 58·2 per cent.
4 grms., similarly treated for twenty days, gave 2·15 grms. residue = 53·7 per cent.

It was noticed that the outer layer of the peel went quite green after about one day, and after about three days the whole went to a brown jelly-like mass, which probably retarded the action; this might perhaps be overcome by using a greater volume of acid.

Alkaline Hydrolysis.

Fifteen grms. of the peel were boiled for half-an-hour with 1 per cent soda, and a deep brown solution was obtained. The residue was collected on a cloth filter, washed, squeezed, and dried; it amounted to 5·05 grms., = 33·6 per cent. 4 grms. of this gave 0·504 grm. hydrazone (when distilled with hydrochloric acid), which corresponds to 6·8 per cent of furfural. The action of the alkali, then, is for the most part progressive dissolution, the inner layer yielding to the action rather more readily than the tougher outer layer.

The solution contained no remainder of oil removable by steam distillation, and gave no precipitate with alcohol either before or after acidifying. Evaporated down on the water-bath, it left an almost black tarry residue.

Dyeing Properties.

A characteristic feature of lignocelluloses is their property of "fixing" certain dyes, and more especially the fixing of a blue cyanide from a mixture of solutions of ferric chloride and alkali ferricyanide. 2·65 grms. inner layer of peel, exposed to the action of a mixture of 30 c.c. each of normal solutions of Fe_2Cl_6 and K_3FeCy_6 for forty-eight hours, gave a blue residue which, on washing and drying, weighed 2·90 grms. Increase, 9·4 per cent (on original).

Owing to the author's lack of time, only the results of the above incomplete investigation can at present be recorded.

Merchant Venturers' Technical College,
Bristol, April, 1903.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, April 22nd, 1903.

Prof. W. A. Tilden, D.Sc., F.R.S., President, in the Chair.

Messrs. C. H. Lockitt, A. J. Webb, and A. H. Scholefield were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Henry James Aubrey, The Cross, Worcester; George Barger, B.A., B.Sc., 50, Guilford Street, W.C.; Charles Drake Bibby, 69, Queen's Road, Twickenham; H. J. W. Brennand, B.A., M.B., Ch.M., 203, Macquarie Street, Sydney; John Christopher Mann, 9, Lambert Street, Hull.

A ballot for the election of Fellows was held, when the following were subsequently declared duly elected:—Henry Guest Adshead; William Lester St. John Alton; Harford Montgomery Atkinson, B.Sc.; Robert Gordon Bibby; George Neville Blackshaw, B.Sc.; Harry Thornton Calvert, B.Sc., Ph.D.; Ben Caudwell, B.A.; Thomas Divine, M.B., C.M.; Arthur William Eastwood, B.A.; John Percy Edgerton; Alan Fletcher; Henry Gough; George Howsam; Alfred Owen Jones; James Stewart Kerr; William Kirkby; John George Collcutt Lock; Arthur Ernest Pitt; Harold Russell Pitt; George Gilbert Pond, Ph.D.; Robert James Porter; Frederick Robertson; Archibald Louis Robinson, B.A.; Fitzroy Owen Jonathan Roose; Ernest William Sawdon, B.Sc.; George Siddle; Montague White Stevens; Henry Edward Stevenson; Giles Hadden Welsford; James Bates Wilkinson, M.D., C.M.; William Francis John Wood, B.Sc.; Edward Chancey Worden.

Of the following papers, those marked * were read:—

*59. "*The Velocity and Mechanism of the Reaction between Potassium Ferricyanide and Potassium Iodide in Neutral Aqueous Solution.*" By F. G. DONNAN and R. LE ROSSIGNOL.

When potassium iodide and ferricyanide react in neutral aqueous solution, free iodine and potassium ferrocyanide are formed, a definite state of equilibrium being attained. If the free iodine is removed as fast as it is formed by means of sodium thiosulphate solution, the velocity of the direct reaction can be investigated by a method similar to that employed by Harcourt and Esson in their fundamental investigation on the speed of chemical reactions. It was found that the reaction proceeded according to the equation, $-dc/dt = kc_1^2c_2^3$, where c_1 = concentration of ferricyanogen ions, and c_2 = concentration of iodine ions.

The simplest interpretation of this equation is that the primary reaction involves *two* ferricyanogen ions and *three* iodine ions according to the equation—

$$2Fe(CN)_6 + 3I = 2Fe(CN)_6 + I_3.$$

The exponents 2 and 3 of the velocity-equation were determined by separate variations of the ferricyanide and iodide concentrations.

The foregoing account of the mechanism of the reaction does not, however, explain all the experimental results, inasmuch as it gives no explanation of the peculiar fact that although the reaction appears to be bimolecular with respect to the ferricyanogen ions (the concentration of the iodine ions remaining constant), nevertheless, the velocity-coefficient varied with the *initial* concentration of the potassium ferricyanide.

A theory which appears to be capable of giving a quantitative interpretation of all the observed results may be briefly summarised as follows:—

1. The actual reaction is assumed to occur between free *ferric* ions and iodine ions according to the equation,—

$$2Fe + 3I = 2Fe + I_3.$$

2. The ferric ions in question are assumed to result from an extremely small dissociation of the ferricyanogen ions into ferric and cyanogen ions.

3. The degrees of dissociation of the ferricyanogen and ferrocyanogen ions are assumed to be the same, or practically the same, in solutions containing the same number of equivalents.

DISCUSSION.

Sir WILLIAM RAMSAY said that Mr. Le Rossignol's reaction was the first quinquemolecular reaction which, so far as he knew, had been investigated. It might appear almost incredible that free iron ions should exist in a solution of potassium ferricyanide, but it must be remembered that their concentration was so low that the most delicate tests for iron, namely, the ferrocyanide and ferricyanide reactions, failed to detect them. Mr. Le Rossignol had made an experiment in which he had electrolysed some potassium ferrocyanide, and he had obtained, after a long time, a deposition of metallic iron on the cathode; this, of course, might be due to a secondary reaction, but, so far as it went, it was in corroboration of the theory.

*60. "*A Microscopic Method of Determining Molecular Weights.*" (A preliminary note). By G. BARGER.

When two solutions of equal vapour tensions, produced by dissolving two substances in the same solvent, are left in a closed chamber, their volumes will not alter after the chamber has become saturated with the vapour of the solvent. If, however, the vapour tensions are unequal, the solvent will distil from the solution with the greater vapour tension into that with the less.

As the result of a suggestion by Prof. L. Errera, of the botanical laboratory of Brussels University, to the effect that this principle might be used for determining molecular weights, the author has elaborated a method, which apparently differs in certain essential features from those hitherto published, and is briefly as follows:—A standard solution of the substance, the molecular weight of which is to be determined, is compared with a number of standard solutions of a substance of known molecular weight.

Small quantities of the two solutions which are being compared are introduced into a capillary tube, where they form bi-concave, discoid drops, care being taken to use the solutions alternately, so that each drop of one solution is enclosed between two drops of the other. The capillary tube is then sealed at both ends, and the length of each drop is measured under the low power of a microscope with the aid of an eye-piece micrometer. After a few hours, or a day, the measurement is repeated, when, if the vapour tensions of the two solutions are unequal, the drops of one series are found to have increased in size, whilst the others have correspondingly diminished.

By using standard solutions of various strengths, an approximate value for the molecular weight is obtained, the limit of accuracy attained at present being about 10 per cent.

The method will undoubtedly be useful in deciding between multiples of an empirical formula in those cases where ebullioscopic methods are not available.

*61. "*Note on the Spectrum of Pilocarpine Nitrate.*" By W. N. HARTLEY.

In the current number of the *Transactions*, p. 452, there is a representation of the absorption curve of pilocarpine nitrate as determined by Prof. Dobbie.

In the author's opinion, the curve is that characteristic of nitric acid, and is only indirectly associated with pilocarpine, certainly not belonging, or peculiar to, this alkaloid. On comparing the diagram with the curve common to nitric acid and potassium nitrate (*Trans.*, 1902, lxxxi., 558), the similarity is easily recognised.

Although there are slight differences of detail in the absorption band, these are due to the recorded measurements not being made at exactly the same points or with solutions of the same concentration, and also in part to a slight modification of the nitric acid curve caused by the pilocarpine molecule.

Pilocarpine, if examined by itself or as a salt of any diactinic acid, such as hydrochloric, acetic, or sulphuric acid, will be found to exhibit no absorption band.

This may be predicted both from the fact that pilocarpine nitrate is highly diactinic, and that stronger solutions than are usually employed were necessary in order to obtain clear indications of the absorption band, and also from the composition and structure of the molecule, the evidence for which is adduced by Dr. Jowett. It is probable that pilocarpine and *iso*pilocarpine are not structurally different, although the manner in which they were examined does not justify the conclusion that their absorption curves are identical. It is not safe to draw inferences from solutions of nitrates of the alkaloids, particularly when the bases themselves exert but little absorption. In such cases, a more searching examination might disclose differences between the alkaloids. As the communication neither refers to the existence of the absorption band of nitric acid nor contains evidence of the absorption caused by pilocarpine and of *iso*pilocarpine alone or in combination with a highly diactinic acid, it might be supposed from a study of the paper that pilocarpine was characterised by an absorption band, but this is certainly not the case. It is evident that, as with caffeine, digitaline, and similar alkaloids (*Phil. Trans.*, 1885, clxxvi., 471), the structure of pilocarpine does not confer on the base any peculiar absorptive power or selective absorption.

DISCUSSION.

Dr. DOBBIE said that the purpose of Prof. Hartley's note was not to call in question the validity of the conclusion that pilocarpine and *iso*pilocarpine are probably isomerides, which had been based on the comparison of their nitrates, but to point out that no information as to the chemical

structure of these bases could be derived from the fact that concentrated solutions of their nitrates showed a well-marked absorption band.

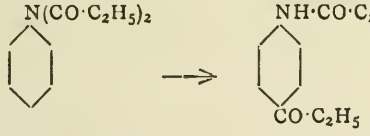
Such bands are usually, in the case of organic compounds, associated with the possession of a benzenoid, pyridine, or similar nucleus, but, inasmuch as nitric acid itself in concentrated solution gives a well-marked absorption band, the presence of a band in the nitrates examined afforded no evidence of the presence of such a nucleus in the alkaloids. The band of pilocarpine, and of *iso*pilocarpine nitrate, occupies the same position, and is very similar to, without being actually identical with, the band of nitric acid. Prof. Hartley regards it as the band of nitric acid modified by the presence of the alkaloid. It is this modification of the band which is of importance in relation to the comparison between pilocarpine and *iso*pilocarpine, instituted in Dr. Jowett's paper. Since the modification is exactly the same in both cases, the conclusion that pilocarpine and *iso*pilocarpine must have the same chemical structure remains unaffected.

In this case, it was necessary to use concentrated solutions of the nitrates for the investigation, because it was found impossible to obtain satisfactory solutions of the free bases.

In the case of alkaloids of high molecular weight, such as berberine, the absorption spectra of dilute solutions of the nitrate are practically the same as those of the chloride, and wholly different from the spectra of nitric acid. Prof. Hartley's caution as to the employment of nitrates in the investigation of chemical structure by the spectroscopic method applies, therefore, more particularly to those highly diactinic substances, which, like pilocarpine, have comparatively low molecular weights.

62. "*Isomeric Change of Dipropionanilide into Propionyl-p-aminopropiophenone.*" By F. D. Chattaway.

Under the influence of various reagents, dipropionanilide, like diacetanilide and dibenzanilide, undergoes transformation into propionyl-*p*-aminopropiophenone :—



Although the *o*-derivative is probably also formed in small amount, only the *p*-derivative can be isolated in quantity. As a catalytic agent, zinc chloride gives the best yield, but hydrogen chloride is also applicable, the transformation being most readily effected by heating propionanilide dissolved in an equivalent amount of propionic anhydride with about one-third its weight of dry powdered zinc chloride for twelve to sixteen hours at 140—150°.

The product, after hydrolysis with alcoholic hydrogen chloride, is rendered alkaline and distilled in steam, the *p*-aminopropiophenone separating from the residual solution in reddish-yellow plates (yield = 50 per cent). The base, which is obtained colourless by crystallisation from alcohol or chloroform, separates in flattened rhombs (m. p. 142°); its acetyl derivative forms colourless, hexagonal prisms (m. p. 175°). Kunckell (*Ber.*, 1900, xxxiii., 2641) describes these compounds as crystallising in yellow needles melting respectively at 140° and 161°.

p-*Aminopropiophenone sulphate*,—

$$(C_2H_5{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2)_2,H_2SO_4,$$

a sparingly soluble salt, forms anhydrous, colourless plates which become red and decompose at 223°; the *platinichloride*, $(C_2H_5{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2)_2,H_2PtCl_6$, forms small, orange-coloured needles.

p-*Acetylchloroaminopropiophenone*,—

$$C_2H_5{\cdot}CO{\cdot}C_6H_4{\cdot}NClAc,$$

colourless plates, m. p. 75°; p-*acetylbromoaminopropiophenone*, short, yellow prisms, m. p. 115°; p-*propionylaminopropiophenone*, $C_2H_5{\cdot}CO{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}C_2H_5$, slender, colourless prisms, m. p. 153°; p-*propionylchloroaminopropiophenone*, $C_2H_5{\cdot}CO{\cdot}C_6H_4{\cdot}NCl{\cdot}CO{\cdot}C_2H_5$, colourless plates, m. p. 80°; p-*propionylbromoaminopropiophenone*, pale yellow, elongated plates, m. p. 120°; p-*benzoylaminopropiophenone*, $C_2H_5{\cdot}CO{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}Ph$, thin, colourless, elongated plates, m. p. 190°; p *benzoylchloroaminopropiophenone*, $C_2H_5{\cdot}CO{\cdot}C_6H_4{\cdot}NCl{\cdot}CO{\cdot}Ph$, colourless plates, m. p. 70°; p-*benzoylbromoaminopropiophenone*, bright yellow, rhombic plates, m. p. 111°.

When heated quickly, the nitrogen-halogen derivatives all undergo transformation at about 200—230° with much decomposition.

63. "*Note on the Formation of Di- and Hexa-methylammonio-cadmium Chlorides.*" By W. R. Lang.

Dry methylamine and cadmium chloride react at −11°, but not at −80°, to form a white powder, corresponding with the formula $CdCl_2,6CH_3{\cdot}NH_2$. When heated to 100°, a stable substance is obtained having the composition $CdCl_2,2CH_3{\cdot}NH_2$, its decomposition is not complete at 300°.

PHYSICAL SOCIETY.

Ordinary Meeting, April 24th, 1903.

Mr. T. H. Blakesley, Vice-President, in the Chair.

Mr. W. B. Croft exhibited the following Elementary Apparatus :—

1. A rhombohedron with each side a rhombus ; to show the optic axis of calcite. There is some doubt whether this figure has a distinctive name.

2. Two equal pendulums A and B hanging from an elastic string. An oscillation is given to A ; this movement is taken up by B, all of it ; and A is left to rest. Then A takes it all back, and the alternation continues. It results from this that if A and B both start with oscillations in planes at right angles, each will give its own movement to the other.

3. Newton's rings with a plate and prism as shown in Preston's "Light." Rings may be seen through both of the free sides of the prism at once ; they are oppositely polarised. Another set may be seen by reflexion from one of these sides, red and green, unpolarised.

4. Herschel's Fringes in Fox-Talbot's form with two right-angled prisms. These fringes are at the border between total reflexion and transmission. By turning the apparatus it may be seen that they develop continuously into Newton's rings, with almost perfect achromatism in one portion. Two prisms have been used which are not optically worked. At the position of total reflexion the point of contact is like a piece of soot on silver ; to an observer in the line at right angles it seems like a hole cut in black velvet. There appears to be continuous glass, and not the two surfaces which cause the loss of half a wave. The effect does not seem to be easily produced with optically worked surfaces.

5. Brewster's Bands in thick plates. This apparatus is based on the description in Preston's "Light" ; but it seems to be better to use a large aperture.

A paper on "*Dimensional Analysis of Physical Quantities and the Correlation of Units*" was read by Mr. A. F. Ravenshear.

The object of this paper is to knit together various divergent views which are current on the subject of dimensions. It is shown that while (1) dimensional analysis and the correlation of units of different kinds can be pursued in one direction until, with completed correlation, we arrive at degrees of undifferentiated quantity, a different procedure may be followed which (2) gives rise to various systems of dimensions descriptive of the physical relationships of the quantities treated. The conditions giving rise to dimensional relations are first set out ; and it is

proposed to distinguish the purely quantitative reading of a dimensional formula by enclosing the sign of equality in square brackets thus :—

$$[\text{force}]\,[=]\,[M]\,[L]\,[T^{-2}],$$

and the reading of it as a physical identity or equivalence thus :—

$$[\text{force}] \equiv [M]\,[L]\,[T^{-2}].$$

A criterion for distinguishing quantities which can be regarded as undimensional from those which are essentially dimensional is proposed in the question :—Is the quantity absolutely constant for all substances under all conditions? The dimensional relation $M = L^3T^{-2}$ derived from the law of gravitation, is then justified and is examined at length. This relation, combined with the demand for the complete correlation of all dynamical units, is shown to require the adoption of the convention—

$$[L]\,[=]\,[T]\,[=]\,[M].$$

This result is interpreted by (1) above. Systems of dimensions are next discussed, with the aid of illustrative tables, and it is shown that by employing different physical laws as bases many different systems may be constructed. By comparison of these systems an index law connecting the dimensions of any physical quantity in different systems becomes manifest, viz., the sum of the indices of L, M, and T is always the same for the same quantity in different systems. The dimensions of magnetic quantity in certain different systems are, for example,—

$$L^3T^{-2},\ ML^{-1}T,\ \varkappa L^2T^{-1},\ pk^{-\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{1}{2}},\ \mu^{\frac{1}{2}}M^{\frac{1}{2}}L^{\frac{3}{2}}T^{-1}.$$

It is concluded that the sum of the indices of L, M, and T in k, μ, and other conventionally suppressed quantities must be zero. By reference to the laws of atomic heats and electrolysis, dimensions for temperature and other thermal quantities are found. Excepting as regards suppressed quantities, temperature is found to have the dimensions of E.M.F. The measurement of force by reference to the law of gravitation is shown to rationalise the indices in the dimensions of electrical and magnetic quantities; and the irrationality of the indices in the conventional systems is explained as due to combining inverse square laws with the simple proportionality of the second law of motion. Finally, it is pointed out that matter, as well as direction, may be distinguished in dimensional formulæ, according to whether it enters as gravitating matter (M_g) mass or inertia (M_i), electrodeposited matter (M_z) or otherwise; and the dimensions of electrical resistance are found in terms of quantities thus distinguished in illustration of (2) above.

Mr. R. J. Sowter read a "*Note on Dimensions of Physical Quantities.*"

Mr. Ravenshear has shown that any physical quantity is expressible in terms of the dynamical quantities L, M, and T, in different ways, but that all the various ways are connected with one another by an index law. One interpretation of this is that the dynamical factors are complete in themselves. They express change-ratios, and have no qualitative significance. μ, k, γ, &c., do not contain dynamical factors, but carry with them the physical qualities or characteristics of the quantities associated with them. Any physical quantity, on this hypothesis, is expressible as $Q = N(D^n)q$, where N is a mere number, (D^n) is a dynamical factor indicating a quantitative measurement process, and q is a quality factor of the nature of Q.

Prof. Everett said the possibility of making two fundamental units suffice instead of three, by taking advantage of the law of gravitational attraction, was nothing new, but was expounded and worked out in some of its applications in ordinary text-books. The proposal to diminish the number of fundamental units by making the unit of length proportional to the unit time, simply amounted to the adoption of a fundamental unit of velocity to take the place of a unit length, and was no simplification. The supposed new law of indices appeared to be simply the well known principle by which information as to physical relations could often be deduced from consideration of dimensions; by which, for example, it could be shown that the velocity of sound must vary directly as the square root of elasticity and inversely as the square root of density.

Mr. Price referred to the fact that the author had determined the dimensions of mass in terms of length and time from the equation $f = m^2/l^2$, considering G, the Newtonian constant of gravitation, as a quantity without dimensions. He thought that if all suppressed dimensions were properly introduced and proper attention paid to the direction of vector quantities, then the dimensions of a quantity gave an idea of its nature, and quantities having the same dimensions were identical in their natures.

Prof. S. P. Thompson said he had read the paper through, and thought it brought the subject no further forward. There were several statements which were so surprising that it was necessary to give them consideration. For instance, we were asked to believe that a scalar, like mass, was of the same dimensions and nature as a vector, like length, and that both of these were physically the same as time. There is no distinction at all in the paper between scalars and vectors. The author's criterion for an undimensional quantity was a false one, and led to obviously incorrect results. Taking the formula $F = Ma$, he (Prof. Thompson) said that, using the author's criterion, mass had no dimensions. The criterion also made G, the Newtonian constant, an undimensional quantity. Referring to the equation $Q = N(D^n)q$ given in Mr. Sowter's note, he thought that the right-hand side might contain a fourth letter representing a geometrical operator. Mr. Ravenshear in his paper had retained fractional exponents which were meaningless and could not possibly exist.

Mr. Ravenshear said that much of the criticism appeared to him to be based upon misunderstandings of his position and the propositions he had advanced. He did not think that G necessarily had no dimensions. His contention was that, owing to its universal constancy, to give it dimensions was not logically compulsory, and therefore it was optional to work out the consequences of both alternatives. He would have preferred that Prof. Thompson had criticised his criterion using Joule's equivalent, the example dealt with in his paper. The example used by Prof. Thompson did not satisfy the criterion, since masses might have any magnitude. He had not advocated the retention of irrational indices, but had put in a plea for two or three systems in which all the indices were integral. Prof. Everett had discussed the matter as though a new system of units was being proposed for practical adoption. Mr. Ravenshear said that, on the contrary, his object was merely the logical analysis of the principles underlying the use of units. He had not proposed to use velocity in place of length or time, but contended that a permanent motion furnished in a single standard two units from which all other dynamical units could in principle be derived.

Mr. Sowter said that Mr. Ravenshear had shown an alternative method of rationalising irrational expressions. Referring to Prof. Thompson's observation that the equation $Q = N(D^n)q$ required a further term representing a geometrical operator, he pointed out that if different directions are accounted for by symbols, these take their places in the dynamical or measuring factors (D^n), so that any physical quantity need only be expressed by the three factors set forth. As regards Prof. Everett's remark on the index law, he was aware of the application of dimensional analysis to the solution of certain physical problems, but he was not aware that the index law had been formulated and the deductions based upon it dealt with previously.

ROYAL INSTITUTION.

Annual Meeting, May 1st, 1903.

Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair.

The Annual Report of the Committee of Visitors for the year 1902, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the Report on the Davy-Faraday Research Laboratory of the Royal Institution, which accompanied it, was also read.

Sixty-two new Members were elected in 1902. Sixty-three Lectures and twenty Evening Discourses were delivered in 1902. The Books and Pamphlets presented in 1902 amounted to about 211 volumes, making, with 683 volumes (including Periodicals bound) purchased by the Managers, a total of 894 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland.
Treasurer—Sir James Crichton-Browne.
Secretary—Sir William Crookes.
Managers—Mr. Henry E. Armstrong, Sir Benjamin Baker, Mr. Shelford Bidwell, Sir Alexander Binnie, Sir Frederick Bramwell, Bart., The Hon. Sir Henry Burton Buckley, The Right Hon. The Earl of Halsbury, Dr. Donald William Charles Hood, The Right Hon. Lord Lister, Mr. George Matthey, Mr. Edward Pollock, Sir Owen Roberts, Sir Thomas Henry Sanderson, Sir Felix Semon, and Sir John Isaac Thornycroft.
Visitors—Mr. John B. Broün-Morison, Mr. Horace T. Brown, Mr. Frank Clowes, Dr. James Mackenzie Davidson, Mr. Frederick William Fison, Mr. Francis Fox, Mr. Francis Gaskell, Dr. James Dundas Grant, Lord Greenock, Mr. James E. Horne, Mr. Maures Horner, Mr. Wilson Noble, Mr. Arthur Rigg, Dr. George Johnstone Stoney, and Mr. George Philip Willoughby.

NOTICES OF BOOKS.

Examination of the Atmosphere of the Central London Railway. Reports by the Chemist and the Medical Officer of Health to the London County Council, to which is Appended a Report by Dr. Andrewes. London: P. S. King and Son. 1903. Pp. 21.

From the point of view of the travelling public, it is very satisfactory to know that there is so little fault to be found with the quality of the air in the Central London Railway, better known as the "Twopenny Tube."

The chemist to the London County Council, Dr. Frank Clowes, expresses the opinion that samples of air taken at any point on the railway should not contain more than 8 volumes of carbon dioxide in 10,000 volumes of the air; that is, not more than twice the amount which is generally found in the air of the street. Of the samples collected, about 22 per cent contained less than this amount, and 34 per cent contained less than two and a-half times as much carbonic acid as that found in the outside air.

Contrary to what would be expected, the air of the smoking carriages contained less carbonic acid than those in which smoking does not take place.

We see in Table VI., giving the maximum and minimum amounts of carbonic acid in samples of the air collected in different places on the Tube Railway, that the highest amount, viz., 15·2 per 10,000, was found in the lifts; this is not astonishing considering the manner in which the lifts are generally packed. In the carriages the figures varied from 14·7 to 9·6 per 10,000, figures which compare very favourably with the air found in *empty carriages* on the City and South London Railway, the Metropolitan, and District Railways. In the case of the Metropolitan Railway the air in an empty carriage between Gower Street and Baker Street contained as much as 28·8 parts of carbonic acid per 10,000 parts of air.

It must be remembered, however, that the carbonic acid in the Tube Railway is due entirely to respiration, and for this reason may be regarded as being more unwholesome than that resulting from the combustion of fuel, on account of the bacteria which may be present.

Let us turn, therefore, to the results obtained by Dr. Andrewes from his bacteriological examination of the Tube air.

The plan adopted by Dr. Andrewes was to take twelve samples of air from different parts of the railway and compare them with twelve samples taken at the same times in the fresh air outside. The details of the method adopted were all carefully worked out, and every care taken to ensure accuracy.

Owing to the fact that a large majority of the organisms present in the air do not grow at the body temperature, and that pathogenic microbes grow more rapidly at this temperature than at that of an ordinary room, the totals are taken from the gelatin plates incubated at 20° C., while duplicate plate cultivations in agar were incubated at 37° C. The highest averages are found in the railway carriages, closely followed by the platforms and lifts; the figures are 63·6, 60, and 56 microbes per 5 litres respectively. In the passages and tunnels the numbers were 20 and 17. The highest actual figures found were on a platform and in a carriage, viz., 112 and 103. The highest number found in the outside air was 93, the lowest being found in the quiet parts of Hyde Park and Kensington Gardens, where the number of micro-organisms sank to 2 in 5 litres of air.

Taking the average of all the observations we find that the outside air contained 33·9 microbes, and the Tube air 44·1. This is only a small difference, and is unduly accentuated, we think, by the fact that several of the samples of the outside air were taken from places practically uninhabited, and by no means representing the ordinary conditions of London life. But in spite of this slight bias against the Tube, the results show clearly that there is no cause for alarm or even for uneasiness; no pathogenic species were found, and Dr. Andrewes states that his attention was so constantly directed to their discovery that he feels tolerably sure that none were overlooked in the 600 or so colonies examined.

The absence of streptococci was a surprise in view of their abundance in the human mouth; this fact speaks powerfully in favour of the rule on the Tube, "Please do not Spit." Altogether, the air of the Tube Railway does not compare unfavourably with that known to exist in inhabited rooms generally, and is probably better than the air in most churches, theatres, and large shops.

Yearly Reports of the Royal Higher College of Agriculture of Portici. ("Annali della Regia Scuola Superiore di Agricoltura di Portici"). Second Series, Vol. IV. Continuation of the Annual Reports of the Royal College from 1875-1898. Portici: Premiato Stab, Tipografico Vesuviano. 1903.

The papers included in this volume are principally concerned with agriculture and arboreal matters; there are a few, however, which are more of a chemical nature; among these we may mention one on "The Analytical Examination of the Products of Recent Eruptions of Vesuvius (1891-4 and 1895-99)," by Eugenio Casoria. The analysis of these materials shows the presence of molybdenum, bismuth, cobalt, zinc, and copper, besides the more common constituents, such as lime, potash, silica, iron, and alumina.

There is also another much longer paper, covering 196 pages, by the same author, in which are given the results of many analyses of mineralised waters in the valleys of the Sarno, the Irno, the Scraio near Vico Equeuse, and others from the neighbourhoods of Vesuvius, Flegrea, and Roccamonfina. Two other papers by Ernesto Monaco are entitled "A Cadmiferous Blende from Mount Somma," and "An Arsenical Sulphide from Pozzuoli."

Exercises in Practical Chemistry and Physics. By J. YOUNG, A.R.C.S., F.C.S., Instructor in Chemistry, Royal Military Academy, Woolwich, Second Edition. Revised and Enlarged. Woolwich: F. J. Cattermole. 1903. Pp. 103.

THIS is essentially a laboratory guide, and will be of great assistance to beginners in practical chemistry. The author gives first the reactions of the commoner metals in their regular group order, then the reactions of the acids; this is followed by analytical tables and exercises in simple qualitative and quantitative work.

There are a few technical exercises adapted to the special case of the college at which Mr. Young is the instructor, such as making gun-cotton and picric acid. There is a thorough "business" appearance about the book, the instructions are concise, and no words are wasted in long descriptions.

Acetylene, its Theory and Applications. ("L'Acétylene, Théorie, Applications"). By MARIE AUGUSTE MOREL, Engineer. Illustrated. Paris: Gauthier-Villars. 1903. Pp. 169.

THE acetylene industry may be fairly claimed by English chemists as due to the work of two of their distinguished predecessors, the brothers Davy. Acetylene was discovered by Edmund Davy, Professor at the Royal Society of Dublin, in March, 1836, and the electric furnace, by means of which carbide of calcium is now manufactured on the large scale, is the outcome of the discovery of the voltaic arc by Sir Humphry Davy in 1813.

It was while preparing potassium (also discovered by Sir Humphry Davy) from carbon and carbonate of potassium that Edmund Davy obtained a black residue which when treated with water gave off a hydrocarbon, which was nothing else than acetylene; however, this name was not given to it until the year 1862, when M. Berthelot re-discovered carbide of potassium, and by its means produced acetylene.

In the following years many other chemists occupied themselves with the study of acetylene, and in 1877 it was liquefied by Cailletet; it was solidified by Willson and Suckert in 1895, and in the same year the practical method of preparing this gas was introduced by the decomposition of carbide of calcium by water.

It was at the end of 1892 that M. Moissan described the new electric furnace he had devised in conjunction with M. Violle, in which a temperature of 2500—3000° was obtained with ease; at this latter temperature carbon reduces oxide of calcium rapidly, and the metal unites with the carbon of the electrodes, forming carbide of calcium, liquid at a red heat, and easily collected.

There have been many works written on acetylene and its production, but the one now before us differs from most of its predecessors in that it treats the subject entirely from the scientific point of view, whereas many other authors have obviously had "an axe to grind."

The first two chapters of this volume deal in a general manner with the metallic hydrocarbides. The history, preparation, properties, and applications of carbide of calcium form the subject of Chapter III.

The two following chapters deal with the physical, chemical, and other properties of acetylene, and its numerous applications are passed in review in Chapter VI. Finally, in Chapter VII. the author describes his own researches on apparatus for the production of acetylene gas.

In the theoretical portion of the book the author has described the work done by the large number of scientific men, both French and those belonging to other nations, who have done so much in this connection, and in the practical part he has confined himself to the applications relevant to science, and describes only those apparatus which agree with the conclusions established from theory.

The book is well written, and is worth binding, though it is not provided with an index.

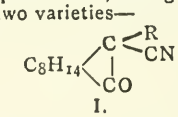
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 13, March 30, 1903.

Affinity at Low Temperatures. Reaction of Liquid Fluorine at −187°.—H. Moissan and J. Dewar.—The affinity of liquid fluorine at a temperature of −187° is powerful enough to ignite sulphur, selenium, phosphorus, and arsenic without the aid of any external energy. It violently decomposes calcium oxide, and with anthracene forms an explosive mixture. Such experiments show that, at very low temperature, the force of affinity acts strongly in reactions as energetic as those between fluorine and certain simple or compound bodies.

Alcoyl and Acylcyanocamphors and Alcoylcamphocarbonic Ethers. Influence of the Double Liaison of the Radicle containing the Asymmetric Carbon on the Rotatory Power of the Molecule.—A. Haller.—In order to examine the influence of the double liaisons on the rotatory power of certain cyclic molecules, the author prepares a number of derivatives of cyanocamphor and submits them to a series of new investigations, by which it is proved that, during their preparation, there are formed the two varieties—



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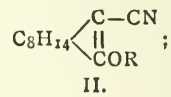

II.

the enolic form (II.) always being present in the largest quantity.

Action of Hydrogen on Arsenic Sulphides in presence of Antimony, and on Antimony Trisulphide in presence of Arsenic.—H. Pélabon.—The author finds that—(1) Antimony completely displaces the arsenic in arsenic sulphide if the two bodies are liquid; (2) hydrogen gas, when heated in presence of antimony sulphide and a mixture of arsenic and antimony, forms sulphuretted hydrogen (the proportion of this latter gas increasing with the amount of arsenic in the preceding mixture); (3) the effect of the arsenic is to decidedly increase the value of the proportion R (the ratio between the partial pressure of the sulphuretted hydrogen and the total pressure of the gaseous mixture); at 625° with pure antimony sulphide and excess of antimony it is the constant number 0·568.

Pyrophosphorous Acid.—V. Auger.—The author succeeds in preparing pyrophosphoric acid by passing the vapour of PCl_3, in presence of a current of CO_2, into the liquid formed by the action of water on excess of PCl_3. The crystals, when purified, are in the form of colourless needles fusing at 38°.

Action of Phosgene on Mixed Organo-magnesium Compounds.—V. Grignard.—The commercial toluenic solution of phosgene, containing 20 per cent of the latter substance, was used to react on organo-magnesium compounds, giving rise to a more or less abundant crystalline precipitate. Theoretically, the reaction can take place in two different ways:—(1) To produce a symmetric

ketone by the reaction of two molecules of the organo-magnesium compound on a molecule of phosgene:— $COCl_2+2RMgX=R-CO-R+2MgXCl$; or, similarly, $ClCOCl+2RMgX=ClC\langle^{R}_{OMgX}+MgXCl$. By treating the resulting products with water in the second case, the unstable $R_2C(OH)Cl$ is obtained, which loses HCl, giving R_2CO. (2) By the action of three molecules of the organo-magnesium compound on one molecule of phosgene a symmetric tertiary alcohol is obtained:— $COCl_2+3RMgX=\frac{R}{R}>C<\frac{OMgX}{R}+2RMgXCl$.

New Researches on the Decomposition of Organic Acids.—MM. Œchsner de Coninck and Raynaud.—The authors continue their researches on the decomposition of the fatty and aromatic acids by treating them at a high temperature with a large excess of sulphuric acid or glycerin. By this means they have more or less verified the stability of the isomeric aromatic acids, and have been able to discover which acids begin to lose carbonic acid at a temperature of about 300°.

Constitution of Nitro-cellulose.—Léo Vignon.—Nitro-celluloses, when reduced by ferrous chloride in acid solution, give rise to oxycellulose. This fact differentiates cellulose decidedly from mannite and from other poly-atomic alcohols which the author has examined from the point of view of nitration.

MISCELLANEOUS.

Royal Institution.—On Saturday next, May 9th, at 3 o'clock, Mr. Hamish MacCunn commences a course of three lectures at the Royal Institution on "Music" (with Musical Illustrations); on Tuesday, May 12th, at 5 o'clock, Prof. G. H. Darwin delivers the first of two lectures on "The Astronomical Influence of the Tides"; and on Thursday, May 14th, Prof. S. H. Vines begins a course of two lectures on "Proteid-Digestion in Plants." The Friday Evening Discourse on May 15th will be delivered by Dr. D. H. Scott on the "Origin of Seed-Bearing Plants," and on May 22nd by Dr. J. A. H. Murray on "Dictionaries."

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. The Chairman announced that His Grace the President had nominated the following Vice-Presidents for the ensuing year:—Sir Benjamin Baker, Sir Frederick Bramwell, Bart., the Right Hon. the Earl of Halsbury, Dr. D. W. C. Hood, the Right Hon. Lord Lister, Mr. George Matthey, Sir James Crichton-Browne (Treasurer), and Sir William Crookes (Honorary Secretary). The special thanks of the Members were returned to Mrs. Frank Lawson for her donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures. The following were elected members:—Mr. W. M. Bird, Sir Edward H. Carbutt, Bart, J.P., Mr. C. Craies, Mr. H. M. Duncan, Dr. A. P. Gould, Mr. J. C. Hawkshaw, Mr. J. G. Hossack, Captain H. A. Johnstone, Lieut.-Colonel W. R. Murphy, Major George J. W. Noble, Mrs. G. J. W. Noble, Mr. H. A. Owen, Mr. C. J. Radermacher, Mr. J. B. L. Stilwell, Mr. R. G. Watt, and A. C. Wombwell.

Memorial to the late Sir Henry Bessemer.—We are requested to announce that a representative Committee has been formed for the purpose of raising a Memorial to the late Sir Henry Bessemer. The phenomenal industrial development of the world in recent years is largely due to the metallurgical process which bears the name of Bessemer, and it has long been felt that his life's work should be suitably commemorated in the centre of the British Empire. The objects of the Memorial are as follows:—

1. The erection (and if necessary the endowment) of Metallurgical Teaching and Research Works in connection with the University of London, equipped for the testing of Ores and Metallurgical Products by modern methods, and for the investigation of new methods and processes.
2. The foundation of International Scholarships for post-graduate courses in practical work in connection with proposals now under the consideration of the Board of Education.

The Committee includes leading representatives of the Metallurgical, Engineering, and Mining Industries and Professions, and of Education Authorities. A Meeting to inaugurate the Fund will be held at the Mansion House on Monday, June 29th next, particulars of which will be published later. All communications should be addressed to the Secretary, Bessemer Memorial Fund, Salisbury House, London, E.C.

"The Etiology of Typhoid Fever."—His Majesty the King has been graciously pleased to accept from Prof. Corfield, M.D., of University College, Consulting Sanitary Adviser to His Majesty's Office of Works, a copy of the Milroy Lectures on "The Etiology of Typhoid Fever," delivered by him before the Royal College of Physicians last year, by special request of the Council of the College; in one of which lectures Dr. Corfield states his opinion that the attack of typhoid fever from which His Majesty suffered in 1871, when Prince of Wales, was not due to any sanitary defects in Londesborough Lodge, Scarborough, the house in which he was staying, and the sanitary condition of which was described by Dr. Corfield in a letter published in *The Times* of January 23rd, 1872, but was no doubt due to contaminated food or drink partaken of by His Royal Highness, the gentlemen of the party, and some of the men servants, away from the house, perhaps at a shooting luncheon, as Her Royal Highness the Princess of Wales, the ladies of the party, and all the female servants escaped infection; the disease, in fact, entirely spared those who were most in the house, and only attacked those who were most away from it, and some of whom did not even sleep there.

A Dust-Arresting Respirator.—The Council of the Society of Arts are prepared to award, under the terms of the Benjamin Shaw Trust, a Prize of a Gold Medal or £20, for the best Dust-Arresting Respirator for use in dusty processes and in dangerous trades. The Council are well aware that for many years past the necessity for such an apparatus has been recognised. As far back as 1822 the Society awarded its Gold Medal to Mr. J. H. Abraham, of Sheffield, for a Magnetic Guard to protect persons employed in dry grinding. The apparatus described in the Society's *Transactions* (1822, vol. xl., p. 135) includes a Respirator to cover the mouth and nose. This Respirator was fitted with magnets, for the purpose of arresting the fine particles of steel thrown off in the process of pointing needles, and in other processes of dry grinding. Although the invention was greatly appreciated at the time, it appears never to have come into practical use, the main objection to it having been, it is believed, raised by the workpeople themselves, who feared that the lessened risk attached to their employment would lower their wages. Similar considerations have, it is believed, stood in the way of the introduction of various appliances intended to limit the risks associated with all trades in which the workpeople breathe a dusty atmosphere. The Council, however, think that such considerations are likely to have less weight at the present time, and they hope that the offer of a prize may draw the attention of inventors to the matter, so that it may result in the production of some suitable piece of apparatus, despite the difficulties with which the solution of the problem is surrounded. The apparatus will be required to fulfil the following conditions:—

1. It must be light and simple in construction:—
2. It should be inexpensive, so as to admit of frequent renewal of the filtering medium or of the Respirator as a whole; or alternatively it should be of such construction that it can be readily cleaned.
3. It should allow no air to enter by the nostrils or mouth except through the filtering medium.
4. It should not permit expired air to be re-breathed.
5. The filtering medium, though it should be effective in arresting dust particles, should not offer such resistance as to impede respiration when worn for some hours under the actual conditions of work.
6. It is desirable that it should be as little unsightly as possible.

It should be noted that the prize is offered for a Respirator intended merely to arrest dust, and not for a chemical Respirator designed to arrest poisonous fumes. The applications of such chemical Respirators are more limited, and there are special requirements connected with them. The Council have, therefore, preferred to limit the range of their present offer to the simpler and more important cases of dust, either dust of all kinds, or of some special character, *e.g.*, iron or steel. Inventors intending to compete should send in specimens of their inventions not later than December 31st, 1903, to the Secretary of the Society of Arts, John Street, Adelphi, London, W.C. Such specimens must be accompanied by full descriptions, and in cases in which the apparatus has been put into actual use, the experience of such use should be given. Competitors intending to patent their inventions should be careful to obtain protection, as the Council of the Society cannot undertake any responsibility as regards the secrecy of the whole, or of any part, of an invention submitted to them. The Prize will be awarded on the report of judges appointed by the Council. The competition is not limited to British subjects. The Council reserve to themselves the right of withholding the Prize, of extending the time for sending in, or of awarding a smaller Prize or smaller Prizes.—HENRY TRUEMAN WOOD, *Secretary*.

The C-acylised Derivatives of the Acetylacetic Ethers.—L. Bouveault and A. Bongert.—The authors describe the preparation and properties of a number of these derivatives, such as the C-butyrylacetylacetate of methyl, the C-isovalerylacetylacetate of methyl, the C-caproylacetylacetate of methyl, and the corresponding ethylic derivatives.—*Bull. Soc. Chim.*, xxvii., No. 20.

The Hydrates $R(OH)_2$.—F. F. Sélivanof.—The author, having observed that freshly precipitated HgO is soluble in a solution of acetamide, but that it is no longer so some time after precipitation, was induced to examine the different metallic hydrates from the point of view of their solubiliiy. The peculiarity shown by HgO may be explained by admitting that $Hg(OH)_2$ is formed first, and that this substance is then transformed into the insoluble HgO; but there are numerous hydrates insoluble in water, but which dissolve in solutions of sugar, glycerin, &c, provided they are in contact with these solutions at the moment of their precipitation; for this reaction it is much more difficult to find an explanation. $Cu(OH)_2$ and $Zn(OH)_2$ are soluble in relatively small quantities of a solution of NH_3, but the solutions may be strongly concentrated over CaO or KOH without a precipitate being formed; finally, $Cu(OH)_2$ gives crystals of $CuO\ 4NH_3.H_2O$; the existence of this already-known compound gives rise to the supposition that copper forms hydrates more hydrated than $Cu(OH)_2$. These higher hydrates are known in the case of many metals, such as Ba, Sr, Ca, Zn, &c. The hydrates $R(OH)_2$ may unite, not only with H_2O, but also with other bases, such as the alkalis, which allows of the supposition that they are able to combine with themselves, forming polymers, $[R(OH)_2]n$. The insoluble hydrates appear to be polymers of this description; this hypothesis finds a basis in the constitution and properties of the basic salts, especially the salts basic to two bases like those which have been produced recently by Mailhe and by Recoura.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., Part 2, p. 13.

MEETINGS FOR THE WEEK.

MONDAY, 11th.—Society of Arts, 8. (Cantor Lectures). "Mechanical Road Carriages," by W. Worby Beaumont, Mem.Inst.C.E.

TUESDAY, 12th.—Royal Institution, 5. "The Astronomical Influence of the Tides," by Prof. G. H. Darwin, F.R.S.

WEDNESDAY, 13th.—Society of Arts, 8. "Preservation of Big Game in Africa," by E. North Buxton.

THURSDAY, 14th.—Royal Institution, 5. "Proteid Digestion in Plants," by Prof. Sidney H. Vines, F.R.S., &c.
—— Society of Arts, 4.30. "The Province of Assam," by Sir James Charles Lyall.

FRIDAY, 15th.—Royal Institution, 9. "The Origin of Seed-bearing Plants," by D. H. Scott, F.R.S, &c.

SATURDAY, 16th.—Royal Institution, 3. "Music" (with Musical Illustrations), by Hamish MacCunn.

UNIVERSITY OF GLASGOW.

LECTURESHIP ON CHEMISTRY AT QUEEN MARGARET COLLEGE.

The University Court of the University of Glasgow will shortly proceed to appoint a LECTURER ON CHEMISTRY to conduct the classes for Women Students in that subject at Queen Margaret College. The appointment will be for five years from October 1st next, at an annual salary of £150.

Candidates should lodge twenty copies of their application and testimonials with the undersigned on or before MAY 30th, 1903.

ALAN E. CLAPPERTON,
Secretary of the Glasgow University Court.

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THE CHEMICAL NEWS.

Vol. LXXXVII., No. 2268.

SOME PHYSICAL PROPERTIES OF NICKEL CARBONYL.*

By JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S., Jacksonian Professor in the University of Cambridge, and HUMPHREY OWEN JONES, M.A., Fellow of Clare College, Jacksonian Demonstrator in the University of Cambridge.

The properties of nickel carbonyl have until recently been the subject of but few investigations. Dr. Mond and his collaborators in the discovery of this remarkable substance determined some of its physical properties, including its boiling-point, specific gravity, and vapour density. Subsequently, Dr. Mond, in association with Prof. Nasini, made observations on its molecular refraction and thermal expansion.

A substance of the peculiar molecular structure of nickel carbonyl seemed to call for further study. The investigation described in the present paper was carried out in the winter of 1901; the authors' intention being to make a complete study of the stability of the compound both in the gaseous and liquid conditions. While the work was in progress a paper by Mittasch was published (*Zeit. Phys. Chem.*, 1902, vol. xl., p. 1) containing an account of an admirable and exhaustive investigation of the velocity of the reaction between nickel and carbon monoxide, including the heat of formation and vapour tensions of the compound, covering part of the ground which we had examined. A number of interesting problems examined in the course of our inquiry however remain, which have not been touched upon by previous investigators, and to some of these the present paper is devoted.

The vapour density of nickel carbonyl was determined by Mond, Langer, and Quincke (*Journ. Chem. Soc.*, 1890, vol. lvii., p. 749) in air at 50° C. by Victor Meyer's method. The value obtained was 86·7, while theory requires 85. The vapour density at this temperature is quite normal, and there is no evidence of association even at this temperature, only some 7° C. higher than the boiling-point of the compound. It was found that the vapour exploded at 60° C. with a flash of light, and carbon dioxide was detected among the products of decomposition. Berthelot (*Comptes Rendus*, vol. cxii., p. 1343) explained the explosion as being due to the production of carbon dioxide by the intermolecular reaction $2CO = CO_2 + C$, which was observed to take place when carbon monoxide acts on nickel at 350—450° C. Later (*Ann. Chem. Phys.*, 1901, [7], vol. xxii., p. 304) it was found that the action only proceeded in this way to a small extent, when nickel carbonyl vapour was decomposed. The reaction $2CO = CO_2 + C$ liberates 38·8 kilogrms. calories, so that if the heat of formation of nickel carbonyl is less than 77·6 kilogrms. calories per molecule; this explanation would be valid. This condition is satisfied since Mittasch (*loc. cit*) has shown that the heat of formation of nickel carbonyl is between 50·6 and 55·6 cals. Hence the detonation observed by Mond might result from the reaction—

$$Ni(CO)_4 = Ni + 2CO_2 + 2C.$$

The fact that nickel carbonyl was thus reported to be explosive, together with the explanation of its explosibility offered by Berthelot, strengthened the belief in its great instability and deterred experimenters from working with it, in any case at temperatures above its boiling-point.

The authors observed that when nickel carbonyl was suddenly heated in an atmosphere of some inert gas, such as hydrogen or nitrogen, the vapour decomposed quietly with deposition of metallic nickel; there was no explosion or flash of light, and the quantity of carbon dioxide produced was so small, in most cases, as to be almost negligible. This was found to be the case even when the temperature used was as high as 130° C. Mittasch (*loc. cit.*) states that he could detect no carbon dioxide when the compound decomposed below 100° C.

The explosion observed by Mond, Langer, and Quincke must therefore have been due to the presence of oxygen, and does not occur in its absence. The amount of carbon dioxide produced by the quiet decomposition is very small, so that the Berthelot reaction, though possible, only takes place to a very slight extent.

It was therefore clear that vapour-density determinations of the compound could be made in atmospheres of inert gases at temperatures much higher than 50° C. As vapour-density determinations of such a unique compound as nickel carbonyl under varying conditions would have a special interest and might well be expected to repay careful study, a large number of vapour-density determinations were made by Victor Meyer's method at temperatures between 63° C. and the boiling-point of naphthalene (216° C.), in order to ascertain the effect of increasing temperature on the dissociation of the compound. The vapour density apparatus was filled in different experiments with various dry inert gases, viz., hydrogen, nitrogen, and ethylene, all carefully purified and especially freed from oxygen.

In order to trace the effect of the rapidity of gaseous admixture on the dissociation, various forms of the vapour-density reservoir were employed. An atmosphere of carbon monoxide was employed to investigate the effect of the gaseous product of dissociation on the stability of the carbonyl.

It was found that the rate of admixture of the vapour with the gases had a marked effect on the dissociation, as shown by the difference in the vapour densities when taken under similiar conditions, in the various inert gases; and, further, that the presence of carbon monoxide produced the expected diminution in the amount of the compound decomposed. In order to further confirm this, two reservoir tubes of different bore were used, one having a cross-sectional area about three times that of the other (the latter will be referred to as the narrow tube) In the latter admixture could take place much less readily than in the former; consequently, the surrounding gas would be expected to have a smaller effect on the extent of the dissociation. This was also confirmed by the experimental results; the vapour density in the narrow tube is almost independent of the gas employed.

The effect of the nature of the surface on the extent of dissociation was tested by using the tubes coated internally with a film of metallic nickel deposited from the vapour of nickel carbonyl by heating. The film of nickel seemed to bring about a state of equilibrium more rapidly, so that the vapour densities determined in these tubes were lower than those in the same tubes not covered by nickel (a similar effect was observed by Mittasch).

It was found that the rate at which the liquid evaporated, as would be expected in the case of a substance which readily dissociates, had some effect on the extent of the dissociation. Hence, it was necessary, in order to get comparable results, to arrange that approximately the same time was taken for vaporisation in all the experiments made at the same temperature. A definite end-point could be observed in each case at which the gas displaced by the vapour ceased to come off, and a much slower evolution of gas took place. The experiment was stopped when the more rapid evolution of gas gave place to the slower.

The results obtained are given in Table I.

In the fourth column the percentages of nickel-carbonyl molecules dissociated are given, calculated from the formula $P = \frac{85 - D}{3D} \times 100$, where 85 is the theoretical vapour density of nickel carbonyl and D is the observed value.

* A Paper read before the Royal Society, March 26, 1903.

TABLE I.—*Vapour Densities Determined by Meyer's Method.*

Temperature of the bulb. °C.	Gas filling the bulb.	Vapour density found (H = 1).	Percentage of $Ni(CO)_4$ dissociated.	Remarks.
63	Nitrogen	83·3	0·7	Very slight deposit of nickel.
		78·2	2·7	Slight deposit of nickel.
64	Hydrogen	79·2		
66	Carbon monoxide	83·9	0·15	Nickel covered tube.
		85·2		
81 (benzene)	Nitrogen	71·0	6·2	Slight deposit of nickel.
		72·1		
100	Hydrogen	67·3	8·8	Nickel deposited over several inches in the tube.
		67·0		
		56·9	16·7	Wide tube covered with nickel.
		56·7		
		79 0	2·4	Narrow tube. Nickel deposit extended about 32 c.m.
		79 8		
100	Nitrogen	70·8	6·7	
		70·9	—	Wide tube.
		75·6	4·1	Narrow tube.
100	Ethylene	70 6	6·8	Wide tube. Nickel deposited over 2 c.m. from bottom of tube.
		70·7		
		73 7	4·3	Wide tube. Moist nickel carbonyl. Nickel deposited irregularly over about 3 c.m.
		76·7		
		77·8	2·7	Narrow tube. Nickel deposit extended 22 c.m.
		79 5		
100	Carbon monoxide	85·0	0·39	Wide tube. No visible deposit of nickel.
		83·1		
		82 6	0·6	Wide tube, covered with nickel carbonyl, dried over phosphorus pentoxide.
		84·5		
		76·4	3·87	Narrow tube. Slight deposit of nickel.
		76·0		
110 (toluene)	Nitrogen	48·4	25·4	Distinct deposit of nickel.
		48·1		
,,	Carbon monoxide	75·2	4·4	Deposit of nickel scarcely visible.
		74·8		
129 (amyl alcohol)	Nitrogen	25·1	76·5	Extensive deposition of nickel over tube.
		26 4		
	Carbon monoxide	31·7	54·5	,, ,,
		32·7		
135 (acetic anhydride)	Carbon monoxide	26·9	72·0	,, ,,
155 (turpentine)	Nitrogen	22·5	94·3	,, ,,
		22 5		
	Carbon monoxide	23 2	—	,, ,,
		23·16	88·8	
182 (aniline)	Nitrogen	23·3	89 0	,, ,,
		23·0		
	Carbon monoxide	24·4	82·8	,, ,,
		23·3	88·2	
216 (naphthalene)	Nitrogen	22·4	93·0	,, ,,
		22·44		
	Carbon monoxide	(20·9)		
		21·3	99·7	

TABLE II.—*Vapour Densities of Nickel Carbonyl by Hofmann's Method.*

Temperature of bath. °C.	Vapour density.	Pressure in m.m. of mercury.	Percentage of nickel carbonyl dissociated.	Percentage dissociated at atmospheric pressure.	
				In nitrogen.	In carbon monoxide.
17	85·6	67·7	0·0		
35 (ether)	81·8	161 4	0 13		
78 (alcohol)	62·6	217·8	11 9	4·1 at 100° C. in narrow tube.	3·87 at 100° in narrow tube.
129 (amyl alcohol)	25·2	389·4	79 1		
	23 8	365·6	85·7	76·5 (wide tube).	54·5 (wide tube).
182 (aniline)	21·5	349·0	98·4		
	20 8	320 6	—	Practically complete in wide tube.	
	21·7	356 0	95·7		

Unless otherwise stated, it is to be understood that the determination was made in a Victor Meyer's apparatus of the usual type, occasionally referred to as the wide tube.

From the figures in the above table, it is seen that the value of the vapour density, deduced from the experiments in the wide tube, is greater in ethylene than in nitrogen and hydrogen. It was also noticed that the deposit of nickel in the latter two gases extended higher up the tube than in the former, and was higher in hydrogen than in nitrogen. In carbon monoxide, on the other hand, the vapour density is higher than in the gases, hydrogen, nitrogen, or ethylene, the values at 100° C. being nearly normal, and the dissociation was incomplete even in aniline vapour. This demonstrates very clearly the effect of the presence of one of the dissociation products on the amount of the dissociation.

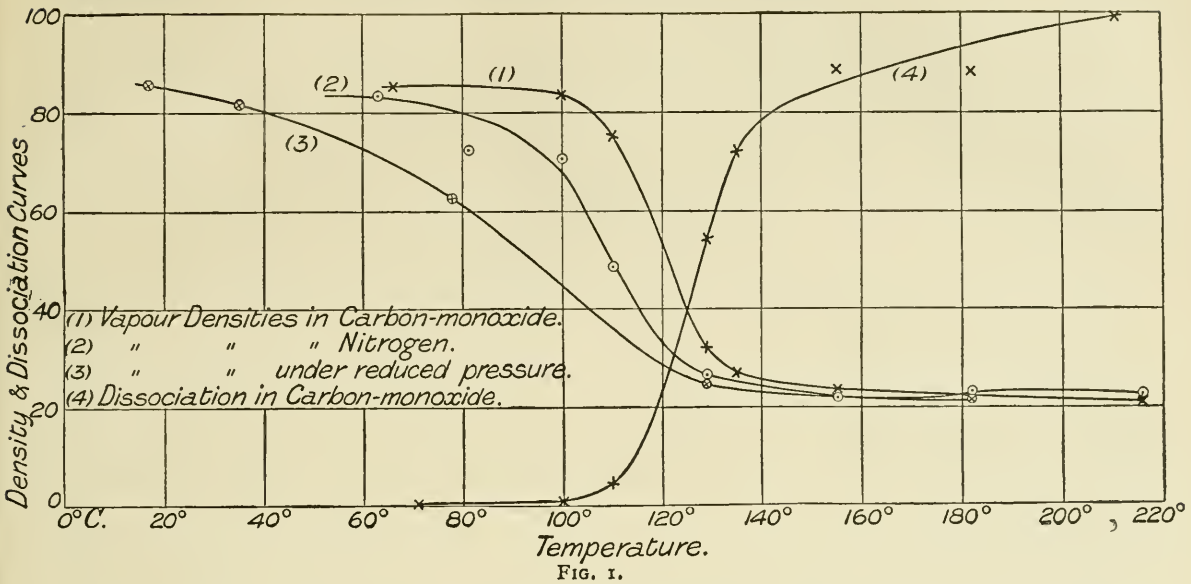


FIG. 1.

In the narrow tube, however, the values obtained at 100° C. do not seem to depend, to any great extent, on the nature of the surrounding gas, the values in carbon monoxide and in the inert gases being almost identical, which shows the great effect of rate of admixture and diffusion on the dissociation.

The amount of dissociation increases rapidly with the temperature; in nitrogen at 155° C. it is practically complete. The rate of increase in carbon monoxide is distinctly slower, the difference between the vapour densities in nitrogen and carbon monoxide at 129° C. being quite marked. Above 155° C. the results obtained are somewhat irregular; but dissociation seems to be nearly complete at atmospheric pressure, since only a small deposit of nickel could be obtained when the tube was placed horizontally and a clear part heated with the blowpipe.

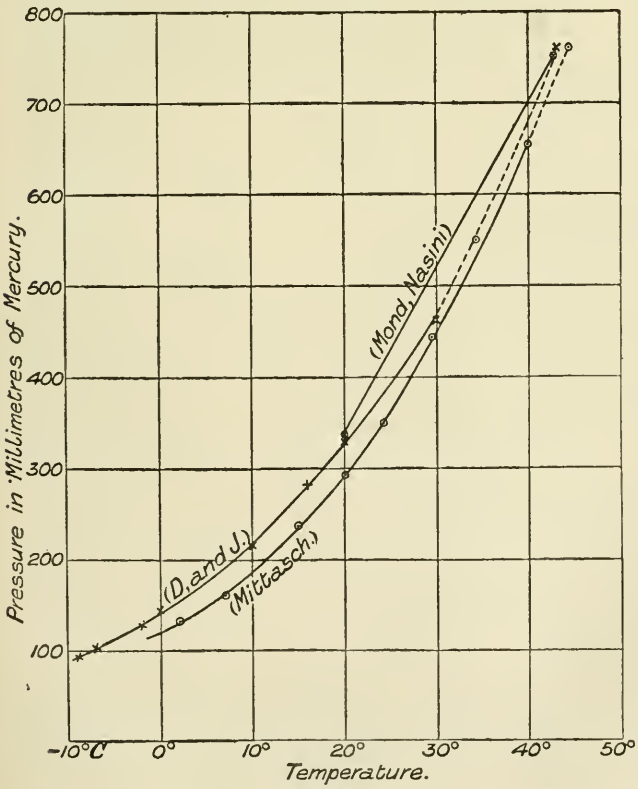


FIG. 2.

A few vapour-density determinations were also made by Hofmann's method at temperatures been 17° C., and the boiling-point of aniline (182° C.), in order to observe the dissociation of the undiluted vapour. Complete dissociation is practically reached at 182° C., but even then the application of a pointed flame to a clear portion of the tube produced a slight deposit of nickel, so that traces of nickel carbonyl were still present.

The results are given in Table II.

The results of the experiments in the narrow tube are given in the fifth column for the sake of comparison, the phenomena in this case being practically the dissociation of the vapour in contact with its own dissociation products. The dissociation is clearly greater under reduced pressure, as might be anticipitated.

The general results of the vapour-density determinations are readily seen from the curves in Fig. 1.

Having thus found that the vapour of nickel carbonyl was much more stable at elevated temperatures than had hitherto been suspected, we resolved to examine the stability of the liquid under pressure, and if possible make observations on it as far as its critical point.

Small sealed tubes from one-half to one-third full of nickel carbonyl were heated to 200° C. without bursting. A small quantity of nickel was deposited on the first heating, and it was found that its quantity was not appreciably increased on repeating the operation. On standing a sufficient length of time at the ordinary temperature the nickel gradually dissolved again, although it was covered by the excess of liquid. This proved in an interesting

manner the ease with which the reaction between the deposited nickel and carbon monoxide is reversible.

The amount of the nickel deposition was notably greater when the liquid was heated in contact with mercury, so that the use of the Cailletet pump for the examination of the critical phenomena was not practicable.

Rough measurements of the critical temperature were made by observing the temperature at which the meniscus disappeared and reappeared, when a quantity of the liquid was alternately heated and cooled in an exhausted and sealed-off piece of glass tube of 2—3 m.m. bore. The tube was heated side by side with a thermometer in a glycerine bath, and was so arranged that it could be inverted at will. The temperatures at which the meniscus disappeared and reappeared, in the course of many repeated observations with different samples of material, ranged between 191° C., and 195° C.

It appears from the observations made with such tubes that the most reliable results were obtained the first time they were heated, the meniscus being better defined and disappearing more sharply than on subsequent occasions. The blurred effect noticed on a repetition of the experiment is due to a somewhat greater amount of carbon monoxide being present.

The presence of carbon monoxide would be expected to cause a lowering of the temperature at which the meniscus disappeared, and this expectation was realised in the course of the experiments. Hence the temperature observed in the first experiment is probably below the true critical temperature. The presence of 4—5 per cent of carbon monoxide with its low critical temperature 128° abs. would be expected to lower the temperature at which the meniscus disappears by about 5° C. That this quantity of carbon monoxide might be present at any time is shown by the following experiment:—

Volume of tube, 1·35 c.c.
,, nickel carbonyl left after heating to 193° C. = 0·437 c.c.
Amount of nickel deposited = 0·0147 grm.
,, carbon monoxide liberated = 0·0284 grm. = 5·02 per cent of the residual nickel carbonyl.

Hence it is very probable that the true critical temperature is about 200° C.

Comparative experiments made with pure ethyl ether in similar tubes gave a critical temperature of 193° C. The accepted value for the critical temperature for ether being 194·5° C., the observed temperature for nickel carbonyl cannot be far removed from the correct value.

The formula $T_b = 0{\cdot}66\ T_c$, where T_b is the absolute boiling-point and T_c the absolute critical temperature, should be applicable to the case of nickel carbonyl, since it is applicable to ether, a liquid which has a critical temperature of approximately the same value. Taking the boiling-point to be 43·3° C., the critical temperature calculated from the above relation would be 201·4° C., which agrees very well with the value which was found as a probable minimum critical temperature.

Although it had not been surmised that nickel carbonyl could ever stand heating above 100° C., nevertheless Mond and Nasini (*Zeit. Phys. Chem.*, 1891, vol. viii., p. 150) calculated the hypothetical critical temperature of nickel carbonyl from the results of their experiments on its coefficient of expansion by means of a formula given by Thorpe and Rücker, and found the value 151° C. In a similar manner Ramsey and Shields (*Journ. Chem. Soc.*, 1894, vol. lxiii., p. 1108) calculated the critical temperature from the temperature coefficient of the molecular surface energy. The value deduced in this way is 182·8° C. It therefore appears that the hypothetical critical temperature calculated by either of these methods falls considerably below its actual value.

Rough indications of the critical pressure were obtained by introducing into the sealed tube containing the nickel carbonyl a small tube of very fine bore, closed at one end and having a small globule of mercury introduced at the other, to act as a manometer. The position of the globule was observed at the ordinary temperature, and again at the critical point. The volume of the air in the small tube occupied about one-thirtieth of its original volume at the latter temperature, so that the pressure in the tube seems to be rather more than 40 atmospheres at the critical point. On cooling, the indicating globule remained permanently displaced some distance up the tube, showing the existence of a pressure developed by the decomposition of the nickel carbonyl. On standing for some time the whole of the nickel disappears, and the carbonic oxide pressure disappears.

The pressure on cooling seemed to be about ten atmospheres, hence the critical pressure would be about thirty atmospheres. Later it will be shown that this is near the actual value.

The critical constants of the compound being known, together with the boiling-point, it is possible to calculate a vapour-pressure curve. It was, however, thought better to determine the vapour-pressure at a number of temperatures below the boiling-point of the liquid, by the static method, and from this curve by extrapolations to deduce the values for higher temperatures.

A wide barometer tube (about 0·7 c.m. diameter) was carefully cleaned, dried and drawn off, to a fine capillary tube at one end. The tube was then placed upright in a vessel of pure dry mercury and exhausted thoroughly with a Fleuss pump. A small tube full of nickel carbonyl was now introduced at the bottom of the tube, and the whole then exhausted again, while surrounded by a freezing mixture, in order to get rid of all adhering air, and finally sealed off rapidly at the fine capillary. By this method of procedure only a very small amount of decomposition took place during the sealing off, as indicated by the very slight deposit of nickel. The pressure was then read off by means of a kathetometer, while the tube was surrounded by a bath kept at various constant temperatures.

The results are appended below, together with those obtained by Mittasch (*loc. cit.*) by the dynamic method.

Dewar and Jones.		*Mittasch.*	
−9° C.	94·3 m.m.	2 05° C.	133·1 m.m.
−7	104·3	7·5	170·5
−2	129·1	15·27	238 2
0	144·5	20·2	294·3
+10	215·0	24·26	349·7
+16	283·5	29·52	444·2
+20	329·5	34·29	532·6
+30	461·9	39·97	647·2

The values for − 9° C. and + 30° C. give the following Rankine formula for the relation between the pressure p in millimetres of mercury and the absolute temperature T. $\log p = 7\,355 - 1415/T$. At 200° C. (about the critical temperature) the pressure calculated from this equation is 30·4 atmospheres. Taking the results obtained by Mond and Nasini, viz., the boiling-point 43° C. 751 m.m., and the pressure at 20° C., 338 7 m.m., a similar expression, $\log p = 7{\cdot}281 - 1392/T$, is obtained.

Taking Mittasch's pressures for 2° C. and 40° C. the Rankine obtained is:—

$$\log p = 7{\cdot}781 - 1555{\cdot}7/T.$$

The boiling-points calculated from these formulæ are given below:—

Mond	43·3° C.
Mittasch	44·4°
Dewar and Jones	43·2°

In order to further confirm our vapour-pressure determinations, we made a determination of the boiling-point of some carefully dried and re-distilled nickel carbonyl. With the barometer at 769 m.m. the liquid boiled at 43·2—43·33° C.

It would therefore appear that our vapour tension curve is the more accurate. The curves, fig. 2, illustrate very

clearly the extent of the deviations at different temperatures.

The latent heat of vaporisation of $Ni(CO)_4$, is 38·1 calories per grm. and the Trouton constant (molecular latent heat divided by the absolute boiling-point) is 20 6, its value for ether being 22. The number obtained by dividing the absolute critical temperature by the critical pressure, which is proportional to the volume of the molecule, Van der Waal's constant *b*, is 15·5; the similar number for carbon monoxide is 3·7, so that nickel carbonyl according to theory has a molecule 4·2 times larger than carbon monoxide. The molecular volume of nickel carbonyl at its boiling-point is 136 as compared with 110 for ether. The critical density appears to be about 0·46, while that of ether is only 0·25. If the liquid densities of Mond and Nasini (*loc. cit.*) are taken with the critical data, then the Waterston formula $v = 2·0398 - 0·5667 \log (198·7 - t)$ fits in very well with the results. A similar formula for ether given by Avenarius is :—

$$v = 3·19 - 0·802 \log (191 - t)$$

The molecular volume of nickel carbonyl at its boiling-point is 136; subtracting from this 7·2 for the nickel atom, we have 32·2 as the volume of each molecule of carbon monoxide in the molecule. Now liquid carbon monoxide at its boiling-point has the molecular volume of 35, so that contraction would take place if liquid carbon monoxide could combine with nickel. The heat of formation of nickel carbonyl is about four times greater than that of the liquefaction of the equivalent amount of carbonic oxide under normal conditions.

The experiments described above show clearly that nickel carbonyl is a substance admirably suited for the demonstration of the phenomena of dissociation. Great care must, however, be taken in handling the substance owing to its poisonous properties when inhaled. It also forms an excellent illustration of a reversible reaction, and the following experiments serve to illustrate the way in which it may be used for this purpose.

A number of carefully dried tubes were exhausted by means of a Fluess pump, and were then filled with a mixture of 10 per cent nickel carbonyl vapour and 90 per cent carbon monoxide, at pressures of 50, 100, 226, 304, 396, 504, and 624 m.m. of mercury respectively. These tubes were then heated in a bath until nickel began to deposit; the tube under observation was then kept at that or a slightly higher temperature for about half-an-hour, and afterwards tested for the presence of nickel carbonyl by heating a clean portion of the tube with a fine pointed flame, and in this way the presence of even a very small trace of nickel carbonyl was immediately detected by the formation of a bright mirror of nickel on the hot part of the tube. The tube at 50 m.m. pressure did not deposit nickel when placed in alcohol vapour; but did so at 100° C., and, after heating for a few hours at this temperature, no nickel carbonyl could be detected in the tube. After standing for a few days, however, nickel was deposited when a clean portion of the tube was heated with a pointed flame, thus showing that nickel carbonyl had been regenerated. In the 100 m.m. tube nickel was still deposited after heating for two days at 100° C.; all the nickel carbonyl was found to have disappeared after the tube had been heated for some time to 130° C. Nickel was deposited in the tube at 226 m.m. pressure at 130° C., in the 301 m.m. tube at 158° C., and in the other tubes at slightly higher temperatures. In the two tubes at the highest pressures there was a considerable quantity of the carbonyl present after heating for an hour at 160° C. All the tubes in which the nickel carbonyl had been so far destroyed that no visible deposit of nickel could be obtained on heating a clean portion of the tube with a small flame, after standing for a few days contained enough of the carbonyl to be readily detected by the above test.

Another form of experiment suitable for demonstration proved the reaction proceeded rapidly at the ordinary temperature, and with a measurable velocity at low temperatures, even when the pressure of the carbonic oxide atmosphere was below 200 m.m. A large bulb of about 200 c.c. capacity was connected to a mercury manometer of small bore (so that the movements of the mercury in the manometer were proportional to the changes of gas concentration in the bulb). The bulb was highly exhausted and then filled with pure nickel carbonyl vapour to a pressure of 51 m.m. of mercury at 15° C. After heating for about an hour to 100° C., the pressure, measured after cooling, had risen to 143 m.m, corresponding to a decomposition of about 60 per cent of the nickel carbonyl present. Heated in a glycerine bath to 154° C., the pressure reached 198 m.m. corresponding to practically complete decomposition, which ought to develope a total pressure of 204 m.m.

On rapidly cooling the bulb and allowing it to stand at the ordinary temperature, the pressure fell, at first, about 3·2 m.m. in an hour, then after two days it had fallen to 120 m.m., or about 55 per cent had re-combined; after four more days the pressure was 97 m.m., or about 60 per cent had re-combined; after standing four weeks some of the deposited nickel remained unattacked.

The bulb was again heated to 150° C. so as to deposit all the nickel on the lower part of the tube, and the pressure now rose again to 200 m.m. The lower part of the bulb where the nickel had deposited, was now immersed in liquid air, when it was observed that still a small but distinct diminution in pressure took place after some hours. Liquid carbonic oxide did not, however, appear to react with nickel reduced from the oxide by hydrogen.

The volatile iron carbonyl has been made the subject of a number of similar observations, dealing with its physical properties and chemical stability, which will be discussed in another communication.

ANALYSIS OF VOLCANIC DUST FROM LA SOUFRIÈRE.

By JOHN BRIDGEFORD COPPOCK, F.I.C., F.C.S.

This dust fell in Barbados on May 7th and 8th, 1902, and was a product of the activity of La Soufrière.

An analysis of the dust yielded the following figures :—

	Per cent.
SiO_2	53·95
TiO_2	0·82
P_2O_5	0·12
SO_3	0·37
Cl	0·22
Al_2O_3	19·21
Fe_2O_3	2·95
FeO	4·78
CaO	8·85
MgO	4·15
Na_2O	3·82
K_2O	0·71
MnO	0·31
	100·26

This analysis was made on material dried at about 120° C.

Traces of copper and nickel are present, but cobalt could not be detected. The presence of a small amount of olivine would account for the presence of copper and nickel. Olivine is characteristic of the St. Vincent volcanoes, which are two near neighbours of La Soufrière; apparently microscopic analysis fails to detect any particles of olivine.

The following physical facts were also determined :—

Average weight of largest particles	0·0001 grm.
Average volume	0·000036 c.c.
Specific gravity	2 6
Magnetic material	3·3 per cent.

Magnetite is a very characteristic constituent of the ash, even perfect octahedra being found.

Science Schools, Stroud, Glos.

THE STRUCTURE OF SPECTRA.*

By Prof. CH. FABRY.

(Concluded from p. 220).

IV. *Satellite Lines.*

THE doublets or triplets of certain metals offer curious peculiarities which merit more than a passing notice.

Take, for example, the mercury spectrum, where we find triplets forming two series, the diffuse series of Rydberg and the fine series. Each triplet of the diffuse series is formed, not of three simple lines, but of several; the first element of the triplet is formed of four lines very close together, the second of three lines, and the third of two. We may look upon each element as being formed of a principal line accompanied by satellites. The same aspect holds good for the other triplets of the series.

On the other hand, the lines of the narrow series appear to be simple lines.

It is quite possible that this simplicity is only apparent, and is due to the fact that the satellites are too close together to be separated with the ordinary spectroscopic apparatus in use. The following facts appear to me to support this opinion. Some years ago, Michelson described a method for obtaining metallic lines of great sharpness by an induction discharge in vapour at low pressure, and at the same time a very accurate interference method to see whether a line is simple, or accompanied by satellites very close to it.†

The position of these satellites remained undetermined up to a certain point; a little later, M. Perot and I published a method by which means these satellites can be seen separately, and which constitutes a complete spectroscopic method more powerful than had been available up to that time. The application of these methods first gave an unexpected result; most of the lines examined by Michelson were shown to be complex; their components, it is true, being too close to each other for the old spectroscopic apparatus to separate them. Of ten metallic lines examined, only two were found to be simple ones. In face of such a proportion it became natural to ask if the fact was a general one, and if the majority of spectral lines dissected, so to speak, by the new methods would all be resolved into clusters of lines. Further observations have not confirmed this fear. Of ten cadmium lines examined by M. Hamy by means of his tubes without electrodes, only the three lines already examined by Michelson were found to be complex. Of eleven lines belonging to different metals examined by M. Perot and myself by means of our spark trembler *in vacuo*, only one copper line was found not to be simple.

Now it happens that it is exactly Michelson's complex lines that belong to Rydberg's narrow series, and it is these that he has examined, as it is in this series that the most brilliant lines of the visible spectrum are found.

Thus, we may take it, at least as a reasonable hypothesis, that all the lines of the secondary series are accompanied by satellites; those of the diffuse series by satellites sufficiently wide apart to be distinguished with the ordinary spectroscopic apparatus; those of the narrow series by satellites very closely placed. All the satellites appear to have the common property of showing a very varied brilliancy according to the conditions of production, such as temperature, pressure, nature of the electric current, &c. There is one fact that M. Perot and I have observed numbers of times in the case of the satellites of Michelson lines, and which is probably true also for the longer known satellites of the diffuse series; one silver line of wave-length 547·2 disappears completely when we use a spark *in vacuo*, while it is of considerable intensity when the spark is produced in air; now this line is a satellite of the line 546·6.

The classification of the lines is not always as complete as in the case of the alkaline metals; with these latter all the lines belong to the three series of pairs; with the other metals there remains a more or less considerable number of lines which are beyond classification. As a general rule the lines which make up the regular series are those which appear at a relatively low temperature (Lockyer's *long rays*); among these are found the spontaneously reversible lines of Cornu. In the spark spectra, which correspond probably to a much higher temperature of emission, the number of lines is considerably greater, and the number of lines classified forms only a small fraction of the total number.

In fact, a certain number of metals give extremely complex spectra of which the lines have escaped classification up to the present; such are the metals of the iron family (Fe, Ni, Co, Mn). Must we admit that their structure is different from that of the metals already examined, or only that the confusion between the series is such that it has not yet been disentangled? The problem would be simplified greatly if we had any criterion by which we could recognise analogous lines.

Their appearance only gives very insufficient data, and we must come to the examination of the properties of the different lines. Up to the present time we know of two phenomena which produce an alteration of the wave-lengths:—Increasing the pressure of the surrounding gas (Humphreys and Mohler) and the production of a magnetic field (Zeeman). The study of these two phenomena is hardly commenced; it has, however, already given very interesting results so far as the classification of the lines is concerned.

V. *Zeeman's Phenomenon.*

The presence of a magnetic field profoundly modifies the emission of light by gases; each line is transformed into a group of lines, differently polarised, and of which the separation goes on increasing with the intensity of the magnetic field. Such is the fact discovered by Zeeman, and which is of such prime importance.

The details of the phenomenon appeared to the first observers who undertook its examination, of an almost discouraging complexity; every line seemed to behave in a different manner without any connection with the conduct of the others. However, the works of Cornu, Michelson, Preston, and especially that of Runge and Paschen, have succeeded in bringing some order out of this chaos, and have reduced them to simple laws, at least for the lines forming part of the regular series.

The different lines forming a definite series behave in an identical manner, so that if we represent each line by its frequency these various lines are transformed in the magnetic field into superposable groups.

Further, there exist simple relations between the manners in which the different series behave. Let us consider an example, taking the spectrum of mercury. The narrow lines of Rydberg form a series of triplets, or, if we prefer it, three parallel series of simple lines which we may call *a*, *b*, and *c*; in each triplet the line *a* is the one with the greatest wave-length. Let us take an *a* line. In the magnetic field perpendicular to the direction of emission, it decomposes into 9 equidistant components symmetrically placed with regard to the original simple line (Fig. 6). These can be designated by the figures 0 (the central line) +1, +2, +3, +4 (on the right), and −1, −2, −3, −4 (on the left). The lines +1 and −1, +2 and −2, &c., are of the same intensity, and are polarised in the same manner. The lines 2, 3, 4, are polarised in the plane of the lines of force; the lines 0, 1, 2, in the perpendicular plane.

* *Revue Générale des Sciences*, Year XIV., No. 5, March 15, 1903.

† A. Michelson "Les Methodes Interferentielles en Métrologie," *Revue Generale des Sciences*, June 30th, 1893, vol. iv., p. 369

One single numerical constant governs the disposition of this complicated group, viz., the distance between two consecutive lines.

The lines *b* and *c* give groups with different aspects, but which may be looked upon as simplifications of the group of nine lines. Without changing the intervals, nor the directions of polarisation, it suffices to modify the intensities of the lines to efface some of them. Fig. 6 gives the form of these groups. To sum up, we may say that all the narrow lines of mercury give, in an equal magnetic field, the same grouping of nine equidistant lines, but differing only in the relative intensities of the different lines; some can be reduced to zero.

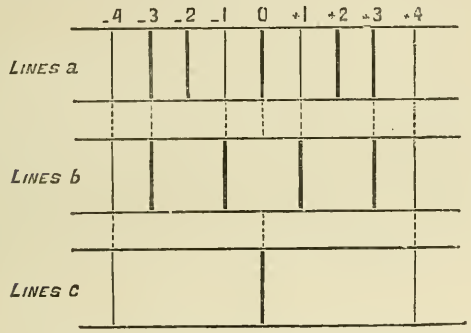


Fig. 6.—Action of a Magnetic Field on the Mercury Lines belonging to the Narrow Series.

Without being able to show in this article, owing to lack of space, the analogous results obtained in other cases, this example should be sufficient to demonstrate the simplicity introduced into the study of this delicate phenomenon, the classification into series. There are many natural families of which the members behave in an identical manner under similar circumstances. We may hope that inversely the study of Zeeman's phenomenon in the cases of spectra not yet disentangled will help us considerably in the recognition of members of the same family. But this is a work that will require a good deal of time, since it is necessary to make an individual and delicate examination of lines which are to be counted by thousands. From this point of view, some interesting results obtained by Messrs. Becquerel and Deslandres on the spectrum of iron, enable us to state that this work will not be unproductive.

The study of Humphreys and Mohler's phenomenon (displacement of lines under the influence of pressure) is still less advanced. We can already foresee, however, that the analogous lines behave in the same manner.

VI. *Absorption Spectra and Band Spectra.*

Kirchoff's law established a connection between emission and absorption spectra; we can make an absorption spectrum correspond in many cases to an emission spectrum, as it is its inverse; or in other words, it is composed of detached lines of darkness on the brilliant background of a continuous spectrum, and occupying the place of the brilliant lines of the emission spectrum.

The material facts which led Kirchhoff to the discovery of the law which bears his name certainly have not changed for thirty years; the two D lines still exist in the solar spectrum, occupying exactly the same place as our two sodium lines; in it we can always find thousands of lines each of which exactly occupies the place of a brilliant line of the iron spectrum, and these facts have lost none of their interest. However, the numerical relationship announced by Kirchhoff does not appear to be so general as it did. Kirchhoff treated as special cases, explicitly excluded from his reasonings, all cases in which bodies are luminous independently of their temperature, in which the radiating energy is obtained from another source than the calorific energy of the body in question. This is the case of a piece of phosphorus exposed to the air, and luminous though cold; it is also the case of phosphorescent and fluorescent bodies.

To-day we give the name of luminescence to all emissions of this nature, reserving that of incandescence for the cases of emission by heat alone (for example, the emission produced by a piece of red-hot iron).

Kirchhoff's reasonings apply to incandescent bodies, and not at all to luminescent ones. Now this, which appeared to be an exception, indeed almost a curiosity, is perhaps, on the contrary, a very frequent case. According to the recent researches of the physicists of the German school, the emission from gases would appear to be due more often to a phenomenon of luminescence than of incandescence. The illumination of a gas by means of electric discharges should in no way be allied with the elevation of temperature (sometimes very problematical) of the gas. A flame of dirty alcohol would be luminescent; that is to say, that pure sodium vapour of the same density and temperature as that existing in the flame should be much less luminous than the former. If this is the case, Kirchhoff's law applied to gases is reduced to this:—If a gas can emit a certain radiation by luminescence, it often happens that it is capable of absorbing it. Perhaps that is not always true, for we know of many beautiful lines which have never been seen reversed.

Inversely, we know of many absorption spectra to which no corresponding emission spectra are known. Such is the remarkable absorption spectrum of oxygen which gives place to the telluric groups A, B, and α of the solar spectrum. Should oxygen heated to above red-heat give the corresponding emission spectrum? It has never been observed, and it is very doubtful.

We may even ask ourselves whether, at a high temperature, the absorption spectrum of oxygen should not disappear. In fact, the little that we know about the absorbent properties of gases seems to indicate that these properties are modified at a high temperature. The vapour of iodine becomes colourless at a red-heat, and there is nothing absurd in the idea that oxygen might cease to absorb the radiations A, B, and α at a sufficiently high temperature.

That would explain the two following facts, which otherwise are contradictory:—The lines A, B, and α seem to be purely telluric, still the existence of oxygen in the sun appears to be thoroughly demonstrated by the presence of black lines which are not telluric in the solar spectrum, corresponding to the lines of one of the emission spectra of this gas, and which should form part of its absorption spectrum at a high temperature.

These absorption spectra, of which we do not know the inverse spectra, are generally band spectra formed of a very large number of lines grouped together in a confined space. Each of these spaces shaded with lines is called a band, but it happens sometimes that the bands, more numerous or closer together, encroach one on the other which gives rise to considerable complications. Often the arrangement of the lines in a band shows remarkable regularity. Fig. 7 shows the absorption band of oxygen, which in the solar spectrum forms the group A.

We observe that the arrangement of the lines justifies the following remark by Langley:—"When, after having looked through the solar spectrum, we meet with one of these groups (A or B), we become conscious of the same feelings that would be experienced by a traveller who, after wandering for a long time in a virgin forest, arrives suddenly at a well laid out park."

Several emission spectra also have this appearance of the bands. Among the most beautiful we may mention the spectra of carbon and of cyanogen, such as are given by the electric arc. The lines are to be counted by the thousand, and they are arranged with remarkable regularity, which does not include extreme complication.

In spite of this regularity, more easy to appreciate than in the line spectra, the band spectra are less well-known,

It is true that the number of lines being much greater, the data take longer to arrange, and the numerical laws have to satisfy much more stringent conditions.

The structure of a band is generally as follows:—It commences brusquely at a point of the spectrum which is called the head or edge of the band. Starting from the edge we first meet with the most brilliant and the narrowest lines; as we get further from the edge the lines become fainter and wider apart. Sometimes, starting from the edge, the lines go towards the red, but more often they extend towards the violet.

With a very slight dispersion, such a group would appear as a band, sharp on one side (the edge) and diffused in the other.

This appearance of the bands reminds us of the arrangement of the series in the line spectra, but with great differences. In the line spectra, the lines also become closer together as we approach the limit of the series; but they appear to be infinite in number with decreasing brilliancy, while in a band, when nearing the head or edge, we find a definite number of lines and increasing brilliancy.

Often from the same edge, not only one, but two or three series of lines start, all situated on the same side of the edge and distributed in an analogous though not identical manner. The result of this is very complicated arrangements of doublets and triplets; if, for example, we have two series starting from the same edge but with slightly different intervals, we should have alternately double and simple lines on account of the mingling of the two series. If there are three series, the complication might become inextricable, the more so as there is no characteristic to distinguish the lines of these three series, each one of which may consist of hundreds of lines. We have seen already in line spectra more than one series converging towards the same limit, but with much less complication, although the number of lines may be infinite.

We need not be surprised, in the face of such complications, that the study of these bands has attracted but few observers.

In a beautiful research on the band spectrum of nitrogen, M. Deslandres has come to the conclusion that in each series the frequencies are to be expressed by a formula of the form $N = a + bm_2$, a and b being two constants, and N the frequency of the line m. In other words, the intervals between successive lines increase in arithmetical progression. From the same edge or head as many as four analogous series may start, but each will have a different coefficient.

Starting from the edge of a band, if we advance on the side where the lines are, we generally find a second edge at a greater or less distance from the former. Sometimes this second edge is so far from the first that the lines of this latter may be already faint, then we can say that there is no confusion; but often this is not the case, and the series starting from the two edges become more or less entangled. Beyond this second edge we may find a third, and so on. All the bands issuing from these various edges form a group of bands, of which the appearance may be most confusing. Again, several observers have determined the exact position of edges which can be recognised easily by means of their greater density, and the increased brilliancy of the lines issuing from them. It is found that the repartition of these edges is analogous to that of the lines of a band. The first edge is the most brilliant, and starting from this one the successive edges become further and further apart.

From the above it is evident that all the lines of a group of bands form a coordinated whole, which we may attempt to represent by a single formula. The simple formulæ, such as those given by M. Deslandres, only give approximate results when the number of lines represented is very great. An attempt at exact representation, made by M. Thiele for one of the carbon bands, led to excessively complicated formulæ, which can only have the value of empirical formulæ.

VII. *Conclusion.*

Whatever results may have been attained up to now, the problem of the repartition of the lines of the spectra is, as we can see, far from being entirely solved. There still remains to be asked, what is the explanation of the experimental laws found, and what are the consequences from the point of view of the emmission theory of light? This theoretical side of the question is as yet hardly touched upon, and we may ask ourselves whether all speculation of this nature would not be premature. Doubtless it would not be impossible to imagine vibrating systems capable of producing the vibrations met with in such or such a spectrum, but would this exercise of the imagination have any notable influence on the progress of spectroscopy.

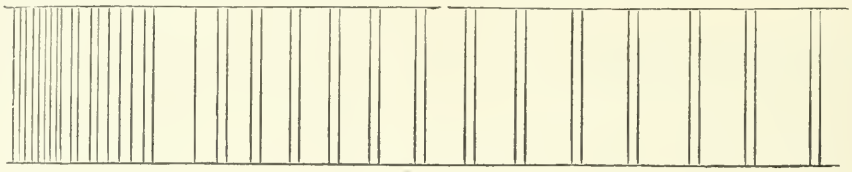


FIG. 7.—ABSORPTION SPECTRUM OF OXYGEN (Band A).

Let us mention some ingenious researches made in this direction by Mr. Johnstone Stoney, who has pointed out some curious relations between planetary movements and those which must be imagined for the purpose of explaining the spectra; in spite of the ingenuity of these relationships we do not see very clearly the cause of these astro-molecular movements.

More recently Mr. W. Sutherland has attempted to connect the laws of regular spectra with the theory of ions, to which Zeeman's discovery brought such striking confirmation. I will only mention these attempts, as I wish here to confine myself entirely to facts.

In the case of absorption spectra, the problem can be presented from another point of view. Although many of these spectra occur in the form of very fine black lines, the absorption is none the less a continuous function of the wave-length, rapidly variable it is true in the neighbourhood of some values.

We could only be really certain of the absorbent properties of a gas if we knew thoroughly the law of the variation of the absorbing power in functions of the wave-length, whereas the position of the black lines only indicates the positions of the maxima of this function. Thus put, the problem becomes closely allied with another, viz., that of abnormal dispersion. The optical properties, relative to a monochromatic radiation, of an isotropic medium are characterised by two constants; its index of refraction, which defines the speed of propagation of the luminous wave, and its index of extinction or its absorbing power which defines the gradual disappearance of this wave as it proceeds. These two quantities are functions of the wave-length.

Numerous researches have shown that neither is independent of the other; the fluctuations of the absorbing power are shown by inflections of the curve of the index. The examination of one of these variable functions cannot

be rationally dissociated from the other. Even the case of ordinary dispersion, that of colourless vitreous substances, can be connected with the latter, as transparent bodies probably only differ from absorbent ones by the particular position of their absorption bands, situated beyond those portions of the spectrum that we can examine most easily. We may hope that the closer study of spectra will one day help to elaborate the theory of dispersion put forward by by Cauchy more than sixty years ago, and not very much advanced to day.

EXPERIMENTS IN FILTRATION.

By GEORGE FREDERICK HORSLEY.

IF two precisely similar precipitates be washed on two precisely similar papers and funnels, for exactly one minute in each case, the one by means of fifty minute additions of water, the other by means of five much larger additions; then, in spite of these different conditions, and in spite of the fact that the total washing liquid used will be quite different in the two cases, still the precipitates will be left contaminated with precisely the same amount of impurity.

The proof consists in an elementary application of the calculus, taking as datum the well-known law of the velocity of fluids in thin tubes. But it depends upon the assumption that the surface of the filter paper is nowhere hindered from fulfilling its function by the enclosing vessel or the contained precipitate, and experiments were accordingly made to test its application under these unfavourable—but practical—conditions.

By making a record of the time when each successive drop of a mixture of ink and water left the funnel, it was easy to obtain remarkably even curves showing the amount of liquid which had passed through the paper at any interval of time after commencing an experiment. It was found that with a strongly ribbed funnel the filtration of ink and water obeys the theoretical law. As the time increases in arithmetical progression, the quantity of liquid contained in the funnel diminishes in geometrical progression. When a plain funnel was used, a deviation occurred, owing to the sides of the paper being impeded as compared with the small open cone at the base. But when a precipitate of ferric hydrate containing 0·1 grm. of iron was placed upon the same filter (an 11 c.m. filter), theory and practice again agreed until the last 20 drops out of a total of 120 drops were reached. These 20 drops, again, filtered rather more quickly than the simple theory would indicate.

Turning now to the application of these results, we see that—

1. If we wish to use the minimum quantity of wash liquid, we must keep the quantity of liquid upon the filter-paper small throughout.

2. The time of working cannot be quickened or delayed by any changes in the method of adding the wash liquid, provided the upper edge of the paper be attended to.

3. If we wish to minimise the drudgery of filtration, we will make each addition as large as possible and allow the precipitate to drain. But the time of washing will not be affected.

Changes of Colour which Mercuric Iodides undergo at Different Temperatures.—D. Gernez.—The author's experiments show that the two varieties of mercuric iodide, when under the influence of refrigerating action, behave as if they were two different bodies, and the quadratic red iodide is not transformed into the orthorhombic yellow iodide. He also finds that these two coloured varieties have clearer and clearer tints as they are cooled—a fact analogous to that recently discovered by M. Moissan with regard to fluorine and sulphur.—*Comptes Rendus*, cxxxvi., No. 14.

NOTICES OF BOOKS.

Determination of Radicles in Carbon Compounds. By H. MEYER. Authorised Translation by J. BISHOP TINOLE. Second Edition, Re-written. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. Pp. xii.—162. 12mo. Illustrated.

DR. MEYER'S "Anleitung zur Quantitativen Bestimmung der Organischen Atomgruppen" met with such success, both in the original language and in translation, that the author was stimulated to prepare this second edition, in which the work has been brought into conformity with the present state of the science by various corrections and additions. In five chapters methods are given, in a compact and useful form, for determination of hydroxyl, of methoxyl, ethoxyl and carboxyl, of carbonyl, and of other groups. Those desirous of making the acquaintance of methods for ascertaining the relative arrangement of the atoms in the molecule of organic bodies will find this little volume a very great help; for a beginner in this study it will be found indispensable.

References to original papers in books and periodicals form an excellent feature of this work, but it is unfortunate that the abbreviations of journal-titles are not more consistently uniform with the list given, and that in the list the requirements of French and German, as respects capitalisation, have not been recognised. This is doubtless due to divided responsibility between author and translator. This small blemish does not, however, detract from the value of the book in the chemical laboratory.

The illustrations, which by the way are not mentioned on the title-page nor in the advertisements, are clear and adequate. H.C.B.

A Handbook of Physics and of Chemistry. By HERBERT E. CORBIN, B.Sc. (Lond.), &c., and ARCHIBALD M. STEWART, B.Sc. (Lond.). With 128 Illustrations. Second Edition. London J. and A. CHURCHILL. 1903. Pp. 438.

ALTHOUGH intended for general use also, the primary object of this book is to enable students to pass the first examination of the Conjoint Examining Board of the Royal Colleges of Physicians and Surgeons.

There is, of course, a good deal to be said in favour of books of this character so long as it is necessary for students to read up for special examinations. They prevent him using up valuable time learning facts which are not wanted in the particular ordeal through which he has to go. Here the necessary knowledge has been abstracted for him from a number of text-books, and has been, so to speak, "peptonised" and served up in an easily assimilable form.

This volume is divided into three principle parts:—(1) Physics, (2) Inorganic Chemistry, and (3) Organic Chemistry; and, considering the size of the volume, a good deal of information has been included in a concise form.

The idea of putting elementary physics first is a good one, as the student will naturally grasp the chemical facts, which are in reality the most important ones, more readily when his mind has been prepared to some extent by acquaintance with some of the fundamental properties of matter. There is an index of eight pages, and the book is well printed and bound.

Die Herstellung von Metallgegenständen auf Elektrolytischem Wege und die Electrograviüre. ("The Production of Metallic Objects Electrolytically and Electro-engraving"). By Dr. W. PFANHAUSER. Halle-a-S.: Wilhelm Knapp. 1903.

As in the case of the earlier volumes of the series of monographs on applied electrochemistry, this book, which is the fifth volume of the series, will undoubtedly have only

a limited number of readers, having been written by an expert for experts, but all engaged in this branch of technology will find in it much to interest them. Though it aims at being merely an extract, by its continual references to and abstracts of original publications, it will be found specially useful in directing the reader to the best source for any detailed information he may require concerning the extension or perfection of existing plant or works. Owing to the unwillingness of many firms to expose secret methods or details and modifications of processes, these cannot always be described as fully as might be desired, and the same applies to the cost of setting up and running the plant. As far as possible, however, full descriptions are to be found here of all the most modern and important developments of the galvano-plastic process, with abstracts of the specifications of German, English, and American patents relating to this branch of electrochemistry. Short accounts of methods of electrolytic etching and Rieder's process of electro-engraving are added.

Das Weltgesetz des Kleinsten Kraftaufwandes in den Reichen der Natur. I. Band. In der Mathematik, Physik, und Chemie. ("The Universal Law of the Least Expenditure of Force in the Realm of Nature." Vol. I. In Mathematics, Physics, and Chemistry). By GUSTAV PORTIG. Stuttgart: Max Kielmann. 1903.

THIS is the first volume of a book which the advertisement tells us is nothing less than epoch-making. It aims at establishing a dualistic theory of the universe as opposed to modern monism. The book is to occupy four volumes, the second dealing with Astronomy, Biology, and the Science of Language; the third with Art and Religion; and the fourth with Philosophy. To attempt a detailed review of this volume would occupy far more space than is at our disposal. Considerable ability is evinced in the treatment of facts and the marshalling of them in array for the purposes of polemics, with an unbounded belief in the theories put forward, and a conviction that from Germany is to be expected the deliverance of the world from the bonds of ignorance, united with a pious dogmatism, which at times produces on the reader an effect startling from its unexpectedness and incongruity. The author is no great respecter of persons or theories other than those he holds. According to him, Hegel is the prince of jugglers, and Leibniz and Kant are not much better. Some parts of his argument are superficial and even trivial, as in the section devoted to mathematics, on the laws of 2 and 3 and their relation to one another, but there is a good deal of shrewd thought exhibited. In places the book is difficult, or rather troublesome, reading; for while no unduly great demand is made on the reasoning powers, the connections between some of the facts and theories are very obscurely stated.

Einrichtungen von Elektrolytischen Laboratorien unter besonderer Berücksichtigung der Bedürfrisse für die Hüttenpraxis. ("The Arrangement of Electrolytic Laboratories, with special reference to the Requirements for Smelting"). By H. NISSENSON. Halle-a-S.: Wilhelm Knapp. 1903.

THIS small book contains descriptions of laboratories devoted to the study and practice of electrolysis, the object of it being to make students and teachers acquainted with the arrangements and appliances in laboratories other than those in which they may happen to have been educated, and at the same time to furnish hints to directors and managers of works, who are supposed not to possess any very extensive scientific knowledge. For this latter purpose a good many elementary facts are detailed in the first part which would probably be perfectly well known by any who are likely to open the book, and might therefore be omitted, or, at any rate, be replaced by references to elementary text books. In the second part are described some of the most important laboratories in Germany, from which a constant stream of distinguished contributions to our knowledge of electrochemistry is issuing. No English laboratory is included among the thirteen described, and only one American, that of the University of Pennsylvania.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

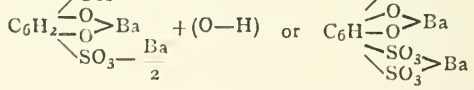
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 14, April 6, 1903.

Derivatives of Plumbic Acid.—Alb. Colson.—The action of chlorine on lead salts in acid solution apparently takes place according to the equation $2Pb(C_2H_3O_2)_2 + 2Cl = PbCl_2 + Pb(C_2H_3O_2)_4$. This reaction gives a method of preparation for tetraplumbic derivatives which is not only advantageous, but which can be applied in cases where the normal salts and the corresponding tetraplumbic salts cannot be separated by difference of solubility.

Preparation of Zinc Sulphide and of Cadmium Sulphide in the Crystalline Form.—Georges Viard.—By passing the vapour of zinc chloride diluted with carbon dioxide over certain metallic sulphides, a crystalline zinc sulphide is formed by double decomposition. Crystalline cadmium sulphide can be prepared by an exactly similar method. The best metallic sulphides to use are tin protosulphide or antimony sulphide.

Action of Alkaline Earth Bases on the Alkaline Earth Salts of the Pyrogallol Sulphonic Acids.—Marcel Delage.—If to a cold aqueous solution of pyrogallol-monosulphonate or disulphonate of barium, strontium, or calcium, there is added gradually, in contact with air, a solution of baryta, strontia, or chalk, coloured substances are produced. The reactions which take place by the contact of these substances are very complex, and the resulting bodies vary generally with the quantity and the nature of the base added, of the salt used, the more or less long contact, the temperature, the nature of the solvent, &c. The coloured substances, however, seem to belong to one of the two types—



Heat of Combustion of Organic Compounds.—P. Lemoult.—The author's experiments on the heats of combustion of certain carbides verify the two following laws:—(1) That isomerous carbides have the same heat of combustion; (2) the difference between two consecutive homologues is 157 cals. He examines sixty cases, and finds in seven (11 per cent) the approximation between the theoretical and measured quantity of heat is less than $\frac{1}{100}$th; in fifteen (25 per cent) it lies between $\frac{1}{100}$th and $\frac{1}{50}$th; in thirty-eight (64 per cent) it is above this limit. He intends to apply the laws to other series of organic compounds.

Nitrated Cellulose.—Léo Vignon.—A divergence is noticed between the maximum of nitration of cellulose obtained from an estimation of the nitrogen without an estimation of the carbon and hydrogen made by various experimenters and the hypothesis that the cellulose molecule exists in the nitrated derivatives obtained. The author fixes $3(NO_3)$ for one molecule in C_6 as the maximum of nitration of cellulose, and he finds that the nitrated derivative obtained is an oxycellulosic derivative.

No. 15, April 14, 1903.

Catalytic Decomposition of Alcohols by Finely-divided Metals. Formenic Primary Alcohols.—Paul Sabatier and J. B. Senderens.—The authors' experiments show that reduced copper is preferable to nickel, cobalt, or platinum for the decomposition of formenic primary alcohols into hydrogen and the corresponding aldehydes. The use of copper affords, therefore, an advantageous method for the preparation of these latter substances. The only practical difficulty in connection with it is the condensation of the aldehydes; these being very volatile substances, a certain proportion being carried away by the evolved hydrogen. In order to make this error as small as possible, the condensation should take place at the lowest available temperature. The authors are further experimenting on the effect of copper on allyl alcohol, benzyl alcohol, and various secondary and tertiary alcohols.

MISCELLANEOUS.

The British Optical Association.—This Association was formed in 1895, primarily with the idea of the encouragement of the science of optics and the art of its application to the improvement of human vision. It was the first Society in the world to institute optical examinations, and at the present day it is the only body in the United Kingdom holding optical examinations which have for their chief subject that of sight-testing. Membership of the Association is obtainable now only by severe examination. The Council have always had one idea in view—legislative powers—not for one, but for all. This is necessary, firstly, for the protection of the public; secondly, for the protection of qualified optologists. To secure legislation there are four essentials:—(1) Classification; (2) Numbers; (3) Influence and Capital; (4) Education by Examination. Classification and numbers will result from the realisation of the scheme now put forward. Influence and capital are at the disposal of the Association, and education by examination has been for some time steadily in practice. To secure representation by numbers it will be necessary to increase the present roll of members by the inclusion of nearly all the optical strength of Great Britain, and it is with this idea in view that the Council asks for co-operation. To be eligible for this register the applicant must have been engaged at least five years as master, assistant, or workman in the selling of spectacles or general optical trade, and he must supply a reference from any one wholesale house; the application form, which is supplied by the Association, to be signed by any member of the firm of that house. The charge for enrolment is purely nominal, viz., 3s. per annum. Further particulars and printed forms of application can be obtained from the Secretary, Mr. John H. Sutcliffe, at the Offices of the Association, 17, Shaftesbury Avenue, London, W.

Hydride of Germanium.—E. Voegelen.—By the reduction of a solution of stannic chloride by means of sodium amalgam, the whole of the tin is not only reduced to the state of stannous chloride, but also partially to the metallic state. With chloride of germanium the reaction is analogous. The metal is precipitated on the amalgam in the form of a greyish-brown deposit. The gas given off burns with a bluish-red flame, and gives metallic stains on cold porcelain. The best results are obtained with the help of zinc and sulphuric acid. The germanium mirror has the following properties:—A lustre similar to that of tin, its colour is green by reflection, and a beautiful red by transmitted light; it is more difficult to volatilise in a current of hydrogen than similar deposits of arsenic; it is difficultly soluble in warm hydrochloric acid; when oxidised with concentrated nitric acid, or even when simply heated in the air, it is transformed into the white binoxide of germanium, soluble in hypochlorite of soda. The binoxide of germanium resulting from the oxidation of germanium can be identified easily by solution in hydrochloric acid and precipitation with sulphuretted hydrogen, which gives a white precipitate of sulphide, soluble in sulphide of ammonium. Hydride of germanium behaves like hydride of antimony with nitrate of silver in solution; it forms a black compound of germanium and silver, attackable by concentrated nitric acid, and depositing binoxide of germanium. The analysis of hydride of germanium has been effected by reacting with it either on an aqueous solution of nitrate of silver or on sulphur. The first method of analysis gives figures for the composition of germanide of silver similar to those required by the formula $GeAg_4$. Those obtained by the second process confirm, in an approximate manner, the formula GeH_4. The following is the equation:—$GeH_4 + S_2 = GeS + H_2S$. Estimations effected on extremely small quantities of material give the atomic proportion $\frac{Ge}{H_4} = \frac{1}{3{\cdot}43}$. Attempts to produce a hydride of tin were unsuccessful.—*Zeit. Anorg. Ch.*, vol. xxx., p. 325.

The Solubility of the Hydrates of the Heavy Metals in Soda.—J. Rubenbauer.—The alkaline solutions of the hydrates of glucinum, zinc, tin (stannous), and lead do not contain combinations in any well-defined proportions, the amount of hydrate dissolved depends considerably on the concentration. With hydrate of zinc (and apparently also with hydrate of glucinum) we obtain only slightly stable solutions, which deposit the hydrate spontaneously on concentration. The influence of the concentration of the alkaline lye on the solubility of the hydrates is relatively small with glucinum and tin, more accentuated with lead, and very great with zinc. There is no proportionality between the concentration of the soda and the solubility of the hydrates. With an appropriate concentration of the alkali we can recognise, in most cases, the existence of either a maximum or of a minimum of solubility. In fact, two factors intervene in these phenomena of solubility; on the one hand, the hydrolysis of the salt formed, zincate, glucinate, &c., a hydrolysis which increases with the dilution; on the other hand, the concentration of the alkali, the solubility diminishing as the concentration increases. This latter action is more difficult to explain, and is caused probably by a dehydration of the hydrates (produced by hydrolysis); these latter are precipitated in a less hydrated form.—*Zeit. Anorg. Ch.*, vol. xxx., p. 330.

MEETINGS FOR THE WEEK

Monday, 18th.—Society of Arts, 8. (Cantor Lectures). "Mechanical Road Vehicles," by W. Worby Beaumont Mem.Inst.C.E.

Tuesday, 19th.—Royal Institution, 5. "The Astronomical Influence of the Tides," by Prof. G. H. Darwin, F.R.S.
— Society of Arts, 4.30. "Mezzotints," by Cyril Davenport, F.S.A.

Wednesday, 20th.—Society of Arts, 8. "Fencing as an Art and as an Historic Sport," by Egerton Castle, M.A.
— Microscopical, 8. Exhibition of Pond Life.
— Chemical, 5.30. "Isomeric Partially Racemic Salts containing Quinquevalent Nitrogen—Part XI., Derivatives of *dl*-Methylhydrindamine and *dl*-Neomethylhydrindamine—Isomeric Salts of the Type $NR_1R_2H_3$," by G. Tattersall and F. S. Kipping. "The Conditions of Decomposition of Ammonium Nitrite," by V. H. Veley. "Note on the Action of Methylamine on Chromic Chloride," by W. R. Lang and E. H. Jolliffe. "The Action of Liquefied Ammonia on Chromium Chloride," by W. R. Lang and C. M. Carson.

Thursday, 21st.—Royal Institution, 5. "Proteid Digestion in Plants," by Prof. Sidney H. Vines, F.R.S., &c. by Sir James Charles Lyall.

Friday, 22nd.—Royal Institution, 9. "Dictionaries," by J. A. H. Murray, M.A., Litt.D., &c.

Saturday, 23rd.—Royal Institution, 3. "Evolution of Music" (with Musical Illustrations), by F. Corder.

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THE CHEMICAL NEWS.

VOL. LXXXVII., No. 2269.

CERTAIN PROPERTIES OF THE EMANATIONS OF RADIUM.

By Sir WILLIAM CROOKES, F.R.S., &c.

THE emanations from radium are of three kinds. One set is the same as the cathode stream, now identified with free electrons—atoms of electricity projected into space apart from gross matter—identical with "matter in the fourth or ultra-gaseous state," Kelvin's "satellites," Thomson's "corpuscles" or "particles"; disembodied ionic charges, retaining individuality and identity.

Electrons are deviable in a magnetic field. They are shot from radium with a velocity of about two-thirds that of light, but are gradually obstructed by collisions with air atoms.

Another set of emanations from radium are not affected by an ordinarily powerful magnetic field, and are incapable of passing through very thin material obstructions. They have about one thousand times the energy of that radiated by the deflectable emanations. They render air a conductor and act strongly on a photographic plate. These are the positively electrified atoms. Their mass is enormous in comparison with that of the electrons.

A third kind of emanation is also produced by radium. Besides the highly penetrating rays which are deflected by a magnet, there are other very penetrating rays which are not at all affected by magnetism. These always accompany the other emanations, and are Röntgen rays —ether vibrations—produced as secondary phenomena by the sudden arrest of velocity of the electrons by solid matter, producing a series of Stokesian "pulses" or explosive ether waves shot into space. These rays chiefly affect a barium platinocyanide screen, and only in a much feebler degree zinc sulphide.

Both Röntgen rays and electrons act on a photographic plate, and produce images of metal and other substances enclosed in wood and leather, and shadows of bodies on a barium platinocyanide screen. Electrons are much less penetrating than Röntgen rays, and will not, for instance, show easily the bones of the hand. A photograph of a closed case of instruments is taken by the radium emanations in three days, and one of the same case by Röntgen rays in three minutes. The resemblance between the two pictures is slight, and the differences great.

The action of these emanations on phosphorescent screens is different. The deflectable emanations affect a screen of barium platinocyanide strongly, but one of Sidot's zinc sulphide only slightly. On the other hand, the heavy, massive, non-deflectable positive atoms affect the zinc sulphide screen strongly, and the barium platinocyanide screen in a much less degree.

If a solid piece of radium nitrate is brought near the screen, and the surface examined with a pocket lens magnifying about 20 diameters, scintillating spots are seen to be sparsely scattered over the surface. On bringing the radium nearer the screen the scintillations become more numerous and brighter, until when close together the flashes follow each other so quickly that the surface looks like a turbulent luminous sea.

It seems probable that in these phenomena we are actually witnessing the bombardment of the screen by the positive atoms hurled off by radium with a velocity of the order of that of light: each scintillation rendering visible an impact on the screen, and becoming apparent only by the enormous extent of lateral disturbance produced by its impact. Just as individual drops of rain falling on a still pool are not seen as such, but by reason of the splash they make on impact, and the ripples and waves they produce in ever-widening circles.

The Spinthariscope.

A convenient way to show these scintillations is to fit the blende screen at the end of a brass tube with a speck of radium salt in front of it and about a millimetre off, and to have a lens at the other end. Focussing, which must be accurately effected to see the best effects, is done by drawing the lens tube in or out. I propose to call this little instrument the "Spinthariscope," from the Greek word σπινθαρίς,* a scintillation.

RADIO-ACTIVE LEAD AS A PRIMARILY ACTIVE SUBSTANCE.

By K. A. HOFMANN and V. WÖLFL.

CONTINUING our earlier communications† we must next call attention to the fact that from different uranium minerals, especially from pitchblende, by ordinary analytical methods, radio-active lead was obtained, its activity originally being about equal to that of the uranium. A decided increase could be obtained, firstly, by extracting the chloride with dilute hydrochloric acid or a slightly acidulated solution of sodium chloride, by which means the activity is concentrated in the most soluble portions, or secondly, and better, by the partial decomposition of the double salt with sodium thiosulphate (*Berichte*, 1902, xxxv., 1453) in aqueous solution, when the sulphides first separating out are most active. By these methods preparations are obtained which through a single screen of quantitative filter-paper affect the electroscope 1000 times as strongly as uranous-uranic oxide, but still contain much ordinary lead. To remove this, the enriched chloride, obtained as described above, is digested with 4 per cent hydrochloric acid, and then a considerable excess of sulphuric acid is added, and alcohol until the liquid contains 30 per cent of it. After once repeating this treatment the residue has an activity (α and β) scarcely greater than that of uranous-uranic oxide, while from the the filtrate, by addition of ammonia and ammonium sulphide, a brown sulphide separates out, which, when dried on the filter, immediately discharges an Elster-Geitel electroscope at a distance of 3 c.m. If, instead of using this method, the sulphate is extracted with dilute aqueous sulphuric acid, the result is only small, as the active sulphate either differs only slightly from ordinary lead sulphate as regards solubility in water, or else is retained by the lead sulphate (especially when this is present in large quantity).

The treatment here given of the chloride with hydrochloric acid and alcoholic sulphuric acid recalls Classen's ("Select Methods of Analytical Chemistry," I., 1901, 106) directions for separating lead and bismuth, so that it might appear that the active constituent is closely allied to bismuth. But in contradistinction to bismuth sulphide, the ammonium sulphide precipitate mentioned above is decomposed by dilute hydrochloric acid at the ordinary temperature, and after evaporation to dryness on the water-bath the chloride is completely dissolved in 0·3 per cent hydrochloric acid. From the solution by means of sulphuretted hydrogen a blackish-brown precipitate is

* Ἐνθ ἐκ νηὸς ὄρουσεν ἄναξ, ἑκάεργος Ἀπόλλων,
ἀστέρι εἰδόμενος, μέσῳ ἡματὶ τοῦ δ' ἀπὸ πολλαὶ
σπινθαρίδες πωτῶντο, σέλας δ' εἰς οὐρανὸν ἵκεν'.

(Here from the ship leaped the far-darting Lord Apollo, like a star at midday, while from him flitted scintillations of fire, and the brilliancy reached to heaven).—HOMER'S *Hymn to Apollo*, lines 440—442.

† *Berichte*, 1900, xxxiii., 3126; 1901, xxxiv., 8, 407, 907, 3033, 3970; 1902, xxxv., 1453. See also K. Hofmann, "Radio-active Substances according to the Present State of Scientific Knowledge," J. A. Barth, Leipzig, 1903.

obtained, which is insoluble in yellow ammonium sulphide, but is very rapidly decomposed by 20 per cent cold hydrochloric acid. The resulting chloride is colourless, crystallises in flat, glittering, double refracting pointed prisms, with direct extinction and beautiful polarisation colours; it differs from polonium in being perfectly soluble in 0·3 per cent hydrochloric acid, gives with potassium iodide a dark yellow (not red, *c.f.* bismuth) iodide, forms white crystals with dilute aqueous sulphuric acid, and on addition of excess of ammonia gives a white turbidity, which on heating forms small glittering white crystals. Hence the substance must first be compared with lead, even if in the precipitation with hydrochloric acid and alcoholic sulphuric acid mentioned above ordinary lead should separate out quantitatively.

The yellowish oxide, which glitters when dry, discharges the electroscope visibly even when present in very small quantity (0·01 gr.), and at a great distance (3 c.m.), and strongly blackens the photographic plate through a double layer of black paper in twenty minutes. Sidot's blende and barium platinum cyanide are rendered highly luminous.

The chloride may be hydrolysed to a very small extent, so that after repeated evaporation to dryness on the water-bath, on extraction with pure hot water, the greatest part of the active constituent remains behind, but it dissolves in 0·3 per cent hydrochloric acid after protracted heating, and is not precipitated from such solution either by water or by alcohol (up to 40 per cent). In this way bismuth (polonium) may be completely, and ordinary lead almost entirely, removed, but the very strongly α- and β-active preparations thus obtained are usually adulterated by an unknown constituent, which has already been mentioned (*Berichte*, 1901, xxxiv., 908, 3036); this colours the chloride pink and the sulphate red at 400°.

Unlike ordinary lead, the active substance is to a very large extent soluble in ammonium carbonate; by the action of oxidising agents, *e.g.*, hydrogen peroxide or bromine, it is concentrated from alkaline solution in the first precipitate.

In the radio-lead preparations, obtained by the methods described above, it may be proved with certainty that they possess primary and not induced activity. This may be deduced from the fact that the sulphate, sulphide, and chloride, after being kept for a year in the dry state, show not a diminished, but in many cases an increased activity towards the electroscope and the photographic plate. Referring to Rutherford's (*Phil. Mag.*, 1903, [6], v., 177) work, for the future, for the sake of brevity of expression, the easily absorbed activity, which is observed by means of the electroscope, and thus increases the conductivity of the air, will be denoted by α, and the activity, which penetrates black paper or aluminium foil, and is demonstrable on the photographic plate, by β.

In contrast to the polonium preparations, whose β-activity very soon disappears, a characteristic property of the radio-lead in the different compounds is the persistence of the β- as well as the α-activity, so that between the poles of a strong magnet, besides the α rays which are either not capable of deflection, or are only slightly deflected in the opposite direction (Rutherford, *loc. cit.*), other strongly deflected rays are always visible on the plate. Nevertheless, as will be shown later, the activity of the lead preparations may be temporarily almost entirely removed, and augmented very considerably by intense cathode rays (K. Hofmann, A. Korn, E. Strauss, *Berichte*, 1901, xxxiv., 407; 1902, xxxv., 1455). According to the most recent work by A. Korn and E. Strauss, which appeared in *Wiedemann's Annalen der Physik*, the β-activity of the sulphate is increased three-fold (as measured by a selenium cell) by cathode rays and also by canal rays, but the α-activity is appreciably strengthened only when it had been previously diminished to a lower value than the normal by chemical changes. This occurs, for instance, on evaporating with sulphuric acid, and on heating to a dull red heat for some hours; the duration of discharge of the original substance is to that of the substance thus treated as forty-five seconds to two minutes. Also by repeated evaporation of the sulphide with hydrochloric acid, solution and re-precipitation with sulphuretted hydrogen, the α-action is temporarily diminished, the duration of discharge prolonged from 65" to 2' 15". After being kept for some weeks the earlier strength is recovered. The β function remains almost unaltered during such changes, which are not accompanied by any separation; though it also may be removed (see later), it is restored in a shorter time (about five days.

The radio-lead salts, therefore, contain a principle giving rise to activity.

As a characteristic of the α-activity the following fact must be mentioned, viz., that by heavy metals of the most different natures the α agent may be removed from the solutions of radio-lead chloride without even a trace of a precipitate being visible on the pieces of metal. When, for example, an aqueous solution of the chloride (α-strength = 20 × uranium) was evaporated on the water-bath four times in a clean platinum dish and then the salt removed, this was decidedly weaker than uranium, though after three weeks the chloride had again attained its former α-intensity (20 × uranium). On the other hand, the platinum dish even after being washed and dried with filter-paper, discharged the end of the wire of the Elster-Geitel electroscope in 5" at a distance of 1 c.m., but after ignition for a quarter of an hour it became quite inactive.

The transference of the α agent from the solution to metals may be observed still better if the latter in the form of little clean strips are suspended in a large quantity (10 litres) of an aqueous saturated solution of radio-active lead chloride. Platinium foil in from two to fourteen days (according to the strength of the lead preparation) thus attains an α-activity which is fifty times as great as that of uranium, without even a trace of a separation being visible. Gold and silver are also strongly charged, but palladium is much superior to all noble metals in this respect, without even the slightest deposit appearing on the clean metal. The presence of hydrogen in the palladium appears to play no part in this characteristic behaviour.

The α-action thus induced persists at the ordinary temperature for months, and is not removed by washing with water and rubbing with paper. It disappears, however, at a red heat in a few minutes.

When the noble metals are immersed in the radio-lead solution the β-activity is taken up to a considerable extent by palladium, but only slightly by platinum. After ignition for half-an-hour it does not disappear, but it is destroyed if the metal is kept for four weeks.

A crystal of bismuth was clean after remaining in the lead chloride solution for eight days, and then appeared only feebly α- and β active, which shows clearly the difference between it and polonium, for in solutions of the latter, according to Marckwald (*Berichte*, 1902, xxxv., 2285), a little stick of bismuth was covered with a black exceedingly strongly α-active deposit.

A lead wire* became strongly α- and less strongly β-active also in the active lead chloride solution, and retained this property after being thoroughly boiled with water and rubbed with filter-paper. By fusion this lead becomes (α) inactive towards the electroscope, but still strongly blackens the photographic plate through opaque paper; this power disappears spontaneously after some weeks.

If a lead wire is immersed to only one-third of its length in the active lead chloride solution, after three weeks the first one-third appears very strongly both α- and β-active; but the parts outside the liquid are far less (α and β) active, and the activity completely disappears towards the free end. The intensity of the α-activity taken up by

* H. Becquerel (*Comptes Rendus*, 1901, cxxxii., 371) was able to render pieces of lead strongly active by induction by means of a radium salt.

the metals mentioned is much greater in the cases of palladium, platinum, silver, and lead than that of the radio-lead salt used for the research. This discharged the electroscope only twice as quickly as uranium, but the palladium foil at a distance of 3 c.m. caused the collapse of the leaves from 120 to 30 volts in one second. The induced silver and lead wire also discharged the electroscope 125 times as quickly as uranium oxide, after being rubbed with filter-paper.

From these researches we can conjecture that the α-agent is a fine material, perhaps consisting of positively charged fragments in Rutherford's (*Phil. Mag.*, [6], v., 177—187) sense, which are occluded like hydrogen by metals, and so may accumulate from a lower to a higher concentration.

The conclusion that in these researches the substance yielding the activity, *i.e.*, the radio-lead itself, is not separated, follows from the fact that the immersed metals remain clean, and are not weakened by rubbing with filter-paper, as well as from the fact that after ignition or being kept for a long time, unlike the radio-lead preparations themselves, they completely lose the α- and β-activity. The *a* agent removed from the solution is again produced in the liquid after some days by the dissolved salt, as special experiments showed.

In order to transfer the β-activity from the radio-lead to other metals to an appreciable extent, an intimate contact of the substances is generally necessary (see above), as, for example, results when they are in the same solution. The platinum metals, especially palladium, platinum, rhodium, and iridium in particular, are separated out in a very strongly α- and β-active condition, after keeping their chlorides in a solution of radio-active lead chloride (about 20 grms. r-$PbCl_2$ to 1 grm. $PtCl_6H_2$) for three weeks by warming with formalin. For instance, the lead chloride used discharged the electroscope from 120 volts to 30 volts in one minute, as compared with uranic-uranous oxide in 1'30", but the iridium which had been rendered active by it discharged the electroscope in five seconds. The platinum metals thus rendered active by induction acted very strongly on the photographic plate through black paper; iridium, for example, fifty times more strongly than uranic-uranous oxide, even if the inducing radio lead chloride only possessed an activity three times as strong as that of uranium. By strongly igniting, the α-activity disappears, but not the β.

Gold, as gold chloride, became very strongly active in four weeks (100 times as strongly as uranium) by induction with thirty times the quantity of lead nitrate, which affected the electroscope twice as strongly as uranium, but after being exposed for fourteen hours to the photographic plate covered with black paper it gave no result, and hence was inactive as regards the β function. Thus the noble metals possess very different powers of taking up the β-activity.

By acting inductively on other substances the lead preparations themselves were temporarily weakened. This occurred in an especially noteworthy manner when a large quantity of ordinary inactive bismuth (about 5 grms.) was mixed with moderately strong radio-lead salt (0·3 grm.). The mixture was evaporated with sulphuric acid, and after three weeks converted into sulphide by potassium sulphide; this was then decomposed by hydrochloric acid, the lead chloride, dissolved in almost pure water, separated from the bismuth oxychloride, and precipitated as sulphide. This lead sulphide after being dried was scarcely active towards either the plate or electroscope, but, after being kept, in six days it regained about two-thirds of its β- and one-third of its α-activity. The bismuth was at first feebly α- and β-active, but after fractional precipitation with water from its solution in hydrochloric acid the first portions separated showed greatly increased activity in both functions.

Hence bismuth is able temporarily to remove the activity from active lead salts (according to experiments which were carried out together with Herr Gonder). On the other hand, it was not found possible conversely to deprive polonium preparations, which are only α-active, of their activity by lead salts (inactive) by the method given above. The bismuth (polonium) retained its α-activity, and there was no indication of its being transformed into β-activity. It certainly seemed *per se* most probable that by mixing much lead salt (inactive) with very strongly α-active polonium, the β-activity, always characteristic of radio-lead salts, would appear. In spite of many experiments this was never observed, from which again the principal difference between radio-lead salts and polonium preparations may be inferred.

Metallic lead on being immersed for twelve hours in a hydrochloric acid polonium chloride solution becomes very strongly α-active, but perhaps, as in Marckwald's (*Berichte*, 1902, xxxv., 2285) experiment, here also it is a question of the precipitation of active metal.

Palladium (*c.f.* Giesel, *Berichte*, 1903, xxxvi., 729), platinum, and silver wire became so strongly α active by means of only α-active polonium solution that they discharged the electroscope in a few seconds, and, especially in the case of palladium, excited Sidot's blende to decided phosphorescence. No decrease of activity was observed in these wires when they were kept for six weeks in a vacuum or in closed tubes. By strongly igniting before the blowpipe this activity disappeared, which, as the persistence of an effect through black paper on the plate showed, consisted only of the easily absorbed α agent. Thus the β-activity had retained its character here also without having experienced any qualitative change in its transference to other metals.

The essential results of this research may finally be given as follows:—There exists a substance analytically closely allied to ordinary inactive lead, but separable from it, which is very strongly primarily active, and produces both α- and β-activity, and hence can act strongly on other metals by induction, whether these are kept as salts in the same solution with the radio-lead chloride, or whether as clean chemically unaltered fragments they are exposed to the influence of the primary agent.—*Berichte der Deutsch. Chem. Gesell.*, 1903, xxxvi., 1040.

THE DETECTION OF SMALL QUANTITIES OF MALTOSE IN THE PRESENCE OF GLUCOSE.

By L. GRIMBERT.

The estimation of a mixture of glucose and maltose does not offer any great difficulty when these two sugars are present in such proportions that the polarimetric deviation and the reducing action can be measured with certainty. The same is not the case, however, when one of the two bodies only is present in very small amount in the mixture. In such a case their transformation into osazone may be of great service.

For this purpose I have endeavoured to make use of the research published by MM. R. Lépine and Boulud in the *Comptes Rendus de la Société de Biologie* of the 7th December, 1901. Their method consists of treating the osazone formed with ether; the maltosazone only went into solution. The evaporated ether left a residue that could be crystallised in warm water; the dried crystals fused at 206°.

I wished, first of all, to verify the value of the method by working on a maltosazone, produced from pure maltose, which had been subjected to two crystallisations in alcohol at 96°, and, to my great astonishment, I found that maltosazone is as insoluble in ether as is glucosazone, which rendered all idea of separation impossible. I must also accept with great reserve the fusion point obtained by the above-mentioned chemists, as they do not give any details as to their method of operating. Now, as has been said truly by L. Maquenne ("Les Sucres et leur Principaux Dérivés," p. 257, 1900), "the fusion-point of

the osazones is not distinctly marked, and may vary even 20° according to the time taken to fuse the material."

Thus, by using an oil-bath and heating rapidly, as recommended by Fischer, I have seen maltosazone commence to decompose at about 180°, while on Maquenne's block, that is by Bertrand's so-called instantaneous method of fusion, a constant fusing-point of 196—198° can be obtained.

Glucose, of which the fusing-point is given at 205°, only fuses at 230—232°, according to Bertrand.

I have therefore taken up the examination of maltosazone and compared its properties with those of glucosazone with the object of finding a means of separating the two.

Maltosazone.—Solutions of pure maltose, more and more dilute, are treated with 1 c.c. of freshly re-distilled phenylhydrazine and 1 c.c. of acetic acid, for each 20 c.c., then heated on the water-bath for one hour. No crystallisation takes place when warm, and the osazone is only formed on cooling.

The reaction is still distinct in a solution containing only $\frac{1}{1000}$th part of maltose; beyond that point I obtained only negative results. In this respect the detection of maltose by phenylhydrazine is less sensitive than that of glucose, of which one part in 20,000 can be detected by this method.

If examined under the microscope immediately it has been prepared, maltosazone appears in the form of large, elongated, tabular crystals of a yellow colour. The crystals are smaller when obtained from dilute solutions, while retaining their general appearance. When re-crystallised in water maltosazone gives the same crystals, but they are shorter and grouped together in rosettes or cockades.

Maltosazone is insoluble in benzene and in ether. It dissolves rapidly in warm water and in cold methylic alcohol, in alcohol at 50°, and in a mixture of equal parts of acetone and water.

When purified by treatment with benzene and dried at 100°, it fuses at 196—198° by Bertrand's instantaneous fusion method.

Glucosazone.—Glucose, treated in the same manner, gives a crystallised osazone, which is precipitated when warm, even in solutions containing only $\frac{1}{500}$ of sugar; beyond this limit the precipitation can only be effected by cooling, and the reaction is still distinct with a dilution of 1 part in 20,000.

Under the microscope glucosazone appears in the form of long needles grouped together in branches, or, from dilute solutions, in characteristic bundles.

Like maltosazone, it is insolnble in benzene and in ether; further, it is insoluble in warm water, and in cold methylic alcohol and in dilute acetone. Its fusing-point by Bertrand's method is 230—232°.

Separation of a Mixture of Glucose and Maltose.—The solution containing the two sugars is treated with 1 c.c. of phenylhydrazine and 1 c.c. of glacial acetic acid for each 20 c.c. The whole is boiled for one hour on the water-bath and then allowed to cool completely. The osazone formed is collected and washed with cold water, then, after desiccation, with benzene, until the latter is no longer covered; finally it is dried at 100°. We have then the choice of the two following methods for the separation of the maltosazone:—

1. The purified osazone is triturated in a glass mortar, with the smallest possible quantity of acetone diluted with its own volume of water. Filter. The filtered liquid, left to itself, soon deposits crystals of maltosazone. If we use too much acetone for the amount of maltosazone present in the mixture, the crystallisation will not take place. In such a case it is necessary to let the liquid evaporate in the air in a glass dish until the odour or acetone has disappeared; then pour the cloudy residue into a small test tube and heat gently on the water-bath until it becomes clear; then allow it to cool slowly.

2. The purified osazone is rubbed up with a very small quantity of water and heated on the boiling water-bath for five minutes. Filter rapidly. On cooling, the filtered liquid gives crystals of maltosazone, which can be re-crystallised as has been described above.

By using these two methods concurrently, I have been able to detect maltose distinctly in a solution of $\frac{1}{1000}$th, containing also $\frac{1}{1000}$th part of glucose, and in another solution containing $\frac{1}{2000}$th part of maltose and 1 per cent of glucose.—*Journ. de Pharm. et de Chimie*, Series 7, vol. xvii., No. 5.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, May 11th, 1903.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 196 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 196 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during April was 2·28 inches; the average fall is 1·61 inches, making an excess of 0·67 inch. There was already an excess of 1·05 inches for the first three months of the year, and adding the present one of 0 67 inch we get a total excess of rain of 1·72 inches, or 24·7 per cent on the thirty-five years' average.

It should be pointed out that, with the exception of 0·31 inch, the whole of the rain during April fell on the last six days, so that, generally speaking, April was a dry month.

Our bacteriological examinations of 315 samples taken during the last month have given the results recorded in the following table. Besides these samples we have examined 200 others from special wells, standpipes, &c., making a total of 515 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 23 samples) ..	149
New River, filtered (mean of 60 samples) ..	6
Thames, unfiltered (mean of 24 samples) ..	2820
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 162 samples)	15
Ditto ditto .. .. highest	163
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 23 samples) ..	193
River Lea, from the East London Company's clear-water wells (mean of 23 samples) ..	20

Of the 245 daily samples taken from the filter-wells of the Metropolitan Water Companies, eight samples, or 3·2 per cent, were sterile. There were only five samples, or 2·0 per cent, containing more than 100 microbes, and of

these only one sample contained more than 150 microbes per c.c. The five excess samples contained an average of 122 microbes per c.c.; in March fifteen excess samples contained an average of 136.

In comparison with the month of March analyses, the bacteriological quality of the London Water supply shows considerable improvement, a result which might have been anticipated from the advent of summer, and the improved natural conditions associated with vegetable growth; a state of things which generally improves the quality of the water obtained from such collecting areas as the valleys of the Thames and Lea.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

Conversazione at Burlington House.

The first Conversazione of this season was held at Burlington House on Friday last, May 15th. The guests were received by the President, Sir William Huggins, K.C.B., O.M., &c., and the Society was honoured by the presence of His Royal Highness the Prince of Wales. There was a large number of interesting exhibits comprising a variety of subjects; chemistry, botany, astronomy, electricity, geology, and bacteriology were all well to the fore.

Among the most interesting we may mention an Apparatus for the Detection and Estimation of Minute Quantities of Arsenic in Beer and Brewing Materials, as recommended by a Departmental Committee of the Board of Inland Revenue, exhibited by Prof. T. E. Thorpe, C.B. The apparatus consists of a small glass vessel, open at the bottom, placed within a porous cell, which itself stands in a cylindrical glass vessel surrounded by cold water. A band of platinum encircling the porous cell forms the anode, and the cathode consists of sheet platinum, cone-shaped, suspended in the glass vessel. The electrolyte is dilute sulphuric acid, and the hydrogen and arseniuretted hydrogen generated at the cathode are dried and passed through a heated glass tube, when the arsenic is deposited. The electric current, if taken from the main supply, is reduced to the required intensity by passing through a rheostat consisting of incandescent lamps, and a number of tests can be carried out simultaneously. In the apparatus shown, the charging board was arranged for four tests.

Dr. A. Macfadyen and Mr. S. Rowland showed their Methods of Disintegrating Cells and Micro-organisms and of obtaining their Intracellular Constituents. In the first method the cells are disintegrated by the violent impact of sand particles in the apparatus exhibited. In the second method the use of extraneous disintegrating material is dispensed with, the cells or organisms being disintegrated when in a frozen condition. In the apparatus exhibited the necessary cold and brittleness was secured by the use of liquid air.

Dr. W. Ramsden had some interesting experiments on Surface Membranes, Bubbles, and "Mechanical Coagulation"; and Dr. T. K. Rose showed specimens of Brittle Gold, and photographs illustrating their micro-structure. He finds that the deleterious effects of many impurities are removed by the presence of oxide of copper dissolved in the metal.

Sir William Crookes showed some experiments illustrating the Properties of the Emanations of Radium:—1. Auto-radiographs of Thorium, Uranium, and Radium Minerals. 2. Photographs of Radium Emanations, Deflectable and Non-deflectable by Magnetism. 3. Radiographs of a Closed Case of Instruments; (*a*) by Röntgen Rays; (*b*) by Radium Emanations. 4. Luminous Effects of Radium Emanations; (*a*) Action of Electrons on a Screen of Barium Platino-cyanide; (*b*) Action of Positive Atoms on a Screen of Sidot's Hexagonal Blende. 5. The Photographed Spectrum of Radium. 6. The Spinthariscope.

The auto-radiographs were prepared by placing pieces of the following minerals over a sensitive photographic plate, and leaving them in the dark:—Thorite, torbernite, autunite, alvite, cleveite or broggerite, uranite, arrhenite, yellow wückite, black wückite, euxenite, samarskite, pitchblende, carnotite, chalcolite, fergusonite, orangeite, thorite, and sipilite. After a few days the plate was developed, and all of them were found to have left an impression, the intensity varying with the mineral.

Another interesting item was a cardboard screen, 10 c.m. × 8 c.m., which had been covered with Sidot's hexagonal blende, which is very sensitive to projected atoms but not to electrons; this was painted over with nitrate of radium, the word RADIUM being in the middle; the light from this screen was of considerable intensity, the word RADIUM being very prominent.

Two radiographs were shown of a box of mathematical instruments, one taken by means of Röntgen rays, and the other by placing a piece of nitrate of radium about a foot above the box. In both cases the instruments showed very clearly, but with the radium exposure, though the outlines of the instruments are very sharp, the whole has rather a blurred appearance.

Amongst meteorological instruments, Prof. F. T. Trouton showed a Gravimetric Recording Hygrometer, and an Electrical Dew-point Hygrometer; and Mr. N. Eumorfopoulos exhibited a Callendar's Compensated Barometer in which the readings were multiplied ten times.

Mr. O. W. Richardson showed an Experiment illustrating the Conductivity imparted to a Vacuum by Hot Carbon. The essential part of this apparatus consists of a vacuum tube containing a carbon filament surrounded by a cylindrical electrode from which it is insulated. The carbon filament is heated by an electric current and maintained at a negative potential of 20 volts, when a current of about one hundredth of an ampère passes from the filament to the cylinder. At a somewhat higher temperature the current reaches the value of about half an ampère. There is no current when the filament is positive relative to the cylinder.

Mr. A. E. Tutton, F.R.S., exhibited his "Elasmometer," a new form of interference apparatus for the determination of the elasticity of solid substances. The apparatus is designed to measure the amount of bending suffered by a thin plate of the substance investigated, when supported near its ends against a pair of platinum-iridium knife-edges, under a known weight applied at its centre.

A High Pressure Spark-Gap used in connection with an inductor of the Tesla type, and also in connection with a radiator of Hertzian waves, was shown by the Rev. F. J Jervis-Smith. The inner coatings of an even number of Leyden jars are connected to the secondary of an induction coil, and to a spark gap, consisting of a thick glass globe, furnished with two platinum-faced balls, adjustable for distance. The outer coatings of the condensers are connected to the primary of a inductor of the Tesla type. The discharge at its terminals is augmented, when the air or gas in the spark-gap globe is subjected to pressure by means of a pump. The shape and character of the gap-spark is greatly modified thereby. The discharge readily perforates and cuts plate-glass, placed in oil, with conductors on each side. The discharge also on striking exhausted bulbs having no terminals produces Röntgen rays of sufficient intensity to produce skiagraphy in a few minutes.

During the evening two demons rations were given in

the Meeting Room, viz., Lantern slides illustrative of the Nile Dam Works, by Sir Benjamin Baker, K.C.B., and the Analysis of Explosion-flames by Photography, by Prof. Harold B. Dixon, consisting of:—(1) Photographs of explosion flames, taken on very rapidly moving films, showing the genesis of the explosion-wave as the flame travels from the point of ignition, and the influence of reflections from the ends of the tube, and (2) photographs of sound-waves moving through the explosion-flame, by which the approximate temperature of the flame may be calculated.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, May 7th, 1903.

Prof. H. McLeod, F.R.S., Vice-President, in the Chair.

Messrs. F. H. Lees, R. Seligman, D. J. Williams, G. H. Welsford, and E. Gumersall were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Ernest Bury, M.Sc., Brackley Coke Works, Little Hulton; Thomas Campbell, Rosemount Villa, Queens Road, Bradford; Albert James Carrier, B.Sc., 30, Kingwood Road, Bath; Francis Gerald Harmer, Middle Class School, Leeds; Frank William G. King, 15, Almond Road, Lower Tottenham, N.; Charles E. L. Livesey, St. Bede's Grammar School, Bradford; Charles S. Purcell, 37, Acomb Street, Greenheys, Manchester; Dennis Tyrrell, 182, King Street, Norwich.

The Chairman announced that the Council at its meeting that day had awarded the Longstaff Medal to Professor W. J. Pope, F.R.S., for his researches on the stereo-chemistry of compounds of elements other than carbon.

Of the following papers, those marked * were read:—

*64. "*The Action of Ammonia and Organic Bases on Ethyl Esters of Olefinedicarboxylic and Olefine-β-ketocarboxylic Acids.*" (Part II.). By S. Ruhemann.

The olefine-β-ketocarboxylic esters may be obtained by the action of hydrogen chloride not only on the dry mixture of an aldehyde and a β-ketonic ester, but also on their solutions in alcohol or benzene. In some cases this method may be found more convenient than that recommended by Knoevenagel (*Ber.*, 1896, xxix., 172), according to which aldehydes react with β-ketonic esters in the presence of amines to yield either olefine-β- ketonic esters or saturated diketonic esters, the result depending on the temperature. It has now been found that piperidine, when added to a mixture of ethyl benzoylacetate and benzaldehyde, readily induces the formation not of the saturated diketonic ester, but of the olefine-β ketonic ester, ethyl benzylidenebenzoylacetate, $PhCO\cdot C(CO_2Et):CHPh$.

The author also showed that diethylamine effects, although much more slowly than piperidine, the formation of ethyl benzylideneacetoacetate, and that on adding the base to the alcoholic solution of benzaldehyde and ethyl benzoylacetate, the diketonic ester, $PhCH(CHBz\cdot CO_2Et)_2$, is obtained. This ester melts at 115—116°, the fused product solidifies on cooling, and then melts at 129—130°. These results differ from Knoevenagel's observations, according to which ethyl benzylidenebisbenzoylacetate melts at 95°. The difficulty with which ethyl benzoylacetate yields, with aromatic amines, diketonic esters is attributed to the stereo-chemical influence exercised by the phenyl group of the ester.

The esters of benzylidenebenzoylacetic, *m*-nitrobenzylideneacetoacetic, and *m*-nitrobenzylidenebenzoylacetic acids react with benzamidine in a manner similar to ethyl benzylideneacetoacetate (*Trans.*, 1903, lxxxiii., 374); they lose either the acetyl group as ethyl acetate, or the benzoyl group as ethyl benzoate, and yield dihydrodiphenylpyrimidone, previously described (*loc. cit.*), or its nitro-derivative, $CH_2<^{CH(C_6H_4\cdot NO_2)}_{CO\text{——}N:CPh}>NH$ (m. p. 192—193°).

In the case of the action of benzamidine on ethyl benzylidenebenzoylacetate, it has been found that the benzoyl group is only partially removed, and that, besides dihydrodiphenylpyrimidone, its benzoyl derivative, $PhCO\cdot CH<^{\text{—}CHPh\text{—}}_{CO\cdot N:CPh}>NH$ (m. p. 241—242°), is produced.

Ethyl *m*-nitrobenzylidenemalonate reacts with benzamidine to form $NO_2\cdot C_6H_4\cdot CH<^{CH(CO_2Et)\cdot CO}_{NH\text{——}CPh}>N$ (m. p. 181—182°), a compound which, under the influence of ammonia, undergoes a transformation similar to that of ethyl dihydrodiphenylpyrimidonecarboxylate (*loc. cit.*), and yields dihydro-*m*-nitrophenyl-phenylpyrimidone (m. p. 192—193°).

*65. "*Spontaneous Decomposition of Nitrocamphor.*" By T. M. Lowry.

A quantity of nitrocamphor, prepared in 1898 and purified by re-crystallising once from alcohol, was found to have undergone change, although a smaller specimen, which had been further purified and crystallised from benzene, was unaltered; 175 grms. of the changed material gave 85 grms. of crystalline nitrocamphor and 55 grms. of a neutral substance sparingly soluble in spirit. This product, which melted at 256°, dissolved in acetone to the extent of 3·22 grms. in 100 c.c. of solution at 13° and gave $[\alpha]_D = +33°$ in acetone. The substance is not readily acted on either by boiling hydrochloric acid or by alcoholic potash, but is oxidised to camphoric acid by heating with nitric acid at 100°. Molecular weight determinations in boiling benzene solution showed it to be a trimolecular compound, formed by the condensation of three molecules of nitrocamphor. One atom of nitrogen is eliminated in the condensation, probably as a result of the oxidation of 1 mol. of nitrocamphor to camphoric anhydride, and the analytical data agree with those required by the equation $C_8H_{14}<^{CO}_{CO}>O + 2C_{10}H_{15}NO_3 = C_{30}H_{42}N_2O_8 + H_2O$.

The substance has therefore the composition of a camphoric ester derived from nitrocamphor or one of its isomerides, and has been found to be identical with a *sesqui-camphorylhydroxylamine*,—

$$C_8H_{14}\left[\begin{array}{l} \\ CO\cdot O\cdot N:C<^{C_8H_{14}}_{O\cdot CO} \\ \\ \end{array}\right]_2,$$

prepared from camphoryl chloride and camphoryloxime.

*66. "*β-Bromo-α'-nitrocamphor and β- and π-Bromocamphoryloximes. The Influence of Impurities in conditioning Isomeric Change.*" By T. M. Lowry.

β-Bromo-α'-nitrocamphor, $C_8H_{13}Br<^{CH\cdot NO_2}_{CO}$, prepared by reducing αβ-dibromo-α'-nitrocamphor with alcoholic potash, differs greatly from nitrocamphor, but closely resembles π-bromonitrocamphor.

The *pseudo*-form, $C_8H_{13}Br<^{C:NO_2H}_{CO}$, separates in a pure state when a solution of the nitro-compound in benzene or ethyl acetate is slowly evaporated; it melts with slight decomposition at 132°, crystallises again on cooling, and re-melts at or below 96°. The *normal* form was not isolated; a solution in methyl alcohol when slowly evaporated, gave a mixture of the two forms, and a solution in formic acid underwent isomeric change. A mixture of the two forms, obtained by crystallising from hot alcohol or acetic acid, softened at 100°, melted without decomposition at about 114°, and re-melted sharply at 100°; the latter is therefore the temperature at which the solid *pseudo* form is in stable equilibrium with the liquid mixture. The *potassium* salt of the *pseudo*-

form crystallises from water in glistening needles with $2H_2O$ and is strongly dextrorotatory; the specific rotatory power of the nitro-compound in the salt is $[\alpha]_D = +103°$.

β-Bromocamphoryloxime, $C_8H_{13}Br\begin{<}{C:NOH \\ >O \\ CO}$, prepared by heating the nitro-compound with hydrochloric acid, separates from water in minute needles with $1H_2O$ and melts at 111°. The anhydrous oxime crystallises from benzene in glistening needles; a solution in chloroform saturated at 13° contains 220 grms. in 100 c.c. and gives $[\alpha]_D = +10°$. The *acetyl* derivative crystallises from ethyl alcohol in minute flakes, melts at 112°, and has $[\alpha]_D = +3°$ in acetone. The *benzoyl* derivative crystallises from alcohol in needles, melts at 134°, and has $[\alpha]_D = +11°$ in acetone; unlike nitrocamphor, which gives the camphoryloxime benzoate, the potassium salt of *pseudo-β*-bromonitrocamphor could not be benzoylated by the Schotten-Baumann method.

π-Bromocamphoryloxime, isomeric with the preceding compound, was prepared synthetically from *π*-bromocamphoric anhydride and hydroxylamine, and is identical with the *iso-π*-bromonitrocamphor which Lapworth (*Trans.*, 1896, lxix., 304) obtained by boiling *π*-bromonitrocamphor with hydrochloric acid; the acetyl derivative melts at 171° and the *benzoyl* derivative at 185°.

Freshly prepared solutions of *β*-bromo-*α'*-nitrocamphor exhibit the phenomenon of mutarotation. A solution in benzene of the *pseudo*-form is at first almost inactive (three specimens gave $[\alpha]_D = +2°$, 0°, and $-4°$), but in the course of two or three days the specific rotatory power becomes constant with $[\alpha]_D = -80°$.

The change of rotatory power is not spontaneous, but is conditioned by the presence of traces of impurity.

Three solutions in benzene of a mixture of normal and *pseudo-β*-bromonitrocamphor were prepared; part of each solution was at once transferred from the graduated flask to a tube and examined in the polarimeter, and in each case a gradual change of rotatory power from $-72°$ to $-80°$ was observed during the first twenty-four hours; a few days later, the remainder of the solution in the flask was also transferred to a tube and examined; in one case only had a state of equilibrium been reached, whereas the other two solutions still exhibited their initial rotatory power, although an interval had elapsed three or four times as long as that normally required for the attainment of equilibrium.

Previous observations have shown that normal nitrocamphor does not change spontaneously on dissolution; the facts now recorded show, further, that even when both isomerides are present in solution, equilibrium between them is only established in presence of a catalytic agent, probably an alkali. A final proof is thus afforded that isomeric change, even when it consists merely in the transference of a mobile hydrogen atom, cannot be accomplished within the molecule, and can only be brought about by an intermolecular mechanism, involving at least three molecules and obeying the ordinary laws of chemical change. The phenomena are closely analogous to Baker's observations on the union of hydrogen and oxygen, and are directly opposed to Laar's hypothesis of "tautomerism."

Discussion.

Dr. Lapworth stated that the important observation that mutarotation did not occur in a solution containing a mixture of the two isomeric bromonitrocamphors found a parallel in the behaviour of camphorquinonehydrazone, for the mutarotation of this substance could apparently be arrested by the introduction of an acid at any stage, and therefore when both forms are present.

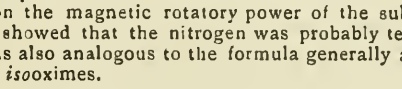
Although Dr. Lowry appeared to conclude that changes of this character were effected by the catalytic agents and would not occur in their absence, yet the usual assumption that the velocity simply becomes immeasurably small in the absence of catalysts seemed to meet the case as well as ever. In the absence of experimental methods for deciding between the two hypotheses, it was impossible to say which view was correct.

Dr. Forster suggested that, in order to avoid confusion arising from the notation of the new derivatives, the name *β*-bromonitrocamphor should be furnished with an affix indicating the position of the nitro-group, and asked whether Dr. Lowry had obtained fresh chemical evidence leading him to continue the representation of the *pseudo*-nitro-group by Hantzsch's original *iso*nitro-formula, which had been abandoned by chemists generally in favour of the nitronic representation.

In reply, Dr. Lowry stated that the rotatory power of the labile solutions was probably not absolutely constant, as it was impossible, in practice, to prepare absolutely pure solutions; in some cases, an appreciable change could be detected, but in others the rotatory power was quite constant within the limits of experimental error. With regard to the notation of the nitro-derivatives, the nitro-group was probably not in the *α*- but in the stereoisomeric *α'*-position. The formula assigned to *pseudo*-nitrocamphor was in accordance with Perkin's observations on the magnetic rotatory power of the substance, which showed that the nitrogen was probably tervalent, and was also analogous to the formula generally adopted for the *iso*oximes.

*67. "*The Electrolytic Reduction of Pheno- and Naphthomorpholones*" By F. H. Lees and F. Shedden.

When phenomorpholone, N-methylphenomorpholone, and N-methyl-*β* naphthomorpholone are electrolytically reduced in sulphuric acid, the first stage of the reduction involves for the most part a disruption of the morpholone ring according to the scheme—



In the case of phenomorpholone, the final products are acetyl *o*-aminophenol, ethyl-*o*-aminophenol, and *isoacetyl-o-aminophenol*, $C_6H_4\begin{<}{OH \\ |\\ N{=}C\cdot OH}^{CH_3}$. The third of these substances crystallises from alcohol in glistening leaflets, and melts at 190° with evolution of water vapour and the simultaneous formation of ethenyl-*o*-aminophenol; this behaviour differentiates it from acetyl *o*-aminophenol, which melts at 205° and is only partially converted into the ethenyl-base at a temperature approaching 300°. The formation of *iso*acetyl-*o*-aminophenol is probably due to the existence in solution of two desmotropic forms of phenomorpholone, these isomerides each undergoing disruption during reduction in accordance with the foregoing scheme.

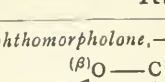
N-Methylphenomorpholone gives N-*acetylmethyl-o-aminophenol*, $C_6H_4(OH)\cdot NMeAc$, which separates from methylal in needles melting at 150°; N-*methylethyl-o-aminophenol*, $C_6H_4(OH)\cdot NMeEt$, the *hydrochloride* of which forms plates melting at 150°; and N-methylphenomorpholine, $C_6H_4\begin{<}{O\text{—}CH_2 \\ |\\ NMe\cdot CH_2}$, which is identical with that obtained by Knorr in another way (*Ber.*, 1889, xxii., 2081).

β.Naphthomorpholone,—

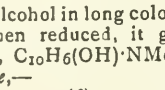
$$C_{10}H_6\begin{<}{{}^{(\beta)}O\text{—}CH_2 \\ |\\ {}^{(\alpha)}NH\cdot CO} \quad \text{or} \quad C_{10}H_6\begin{<}{{}^{(\beta)}O\text{—}CH_2 \\ |\\ {}^{(\alpha)}N:C\cdot OH},$$

was prepared by the reduction of *α-nitro-β naphthoxyacetic acid*, $C_{10}H_6(NO_2)\cdot OCH_2\cdot CO_2H$, the latter being obtained by two methods:—(1) By nitrating *β*-naphthoxyacetic acid; (2) by condensing the potassium salts of *α*-nitro *β*-naphthol and chloracetic acid in aqueous solution. The nitro-acid separates from acetic acid in yellow prisms and melts at 188—189°; the morpholone obtained from the same solvent forms colourless needles and melts at 215—216°.

N-Methyl-β-naphthomorpholone,—



crystallises from alcohol in long colourless needles melting at 84—85°. When reduced, it gives *N-methylethyl-α-amino-β-naphthol*, $C_{10}H_6(OH)\cdot NMeEt$, and *N-methyl-β-naphthomorpholine*,—



The former distils at 193° (corr.) under 40 m.m. pressure, and is a light yellow oil solidifying on cooling to needles which melt at 25—27°; the *sulphocamphylate*, $C_{13}H_{15}ON\cdot C_9H_{14}O_5S,H_2O$, separates from water in prismatic needles melting at 203—204°; the *hydriodide* crystallises from a mixture of acetone and ether in needles which melt at 183°; the *acetyl* derivative, $C_{13}H_{14}N\cdot OAc$, is a colourless oil boiling at 212—215° (corr.) under 40 m.m. pressure. The morpholine distils at 220—222° under 40 m.m. pressure as a viscid, light-yellow oil, having a blue fluorescence and a faintly basic odour; the *sulphocamphylate*, $C_{13}H_{13}ON\cdot C_9H_{14}O_5S,H_2O$, forms needles melting at 196°; the *methiodide*, $C_{13}H_{13}ON\cdot MeI$, separates in needles melting at 163—164° with evolution of methyl iodide.

DISCUSSION.

Mr. GROVES asked whether the authors had tried to reduce morphine electrolytically, and, if so, whether its morpholine ring underwent disruption in the manner observed with pheno- and naphtho-morpholones.

Mr. LEES, in reply, said that in connection with another investigation he had found that morphine is not changed when subjected to electrolytic reduction. Pheno- and naphtho-morpholones are aryloxy-compounds, whereas in morphine the ether-oxygen atom is attached to a partially reduced aromatic nucleus.

68. "*The Coloured Constituents of Butea Frondosa.*" By E. G. HILL.

The dried and fresh flowers of *Butea frondosa* are extensively used in India for the preparation of a somewhat fugitive yellow dye.

The aqueous extract of the flowers contains an easily decomposable tannin which readily yields phlobaphen; this product, which separates from the solution as a dark, tarry precipitate on boiling with hydrochloric acid, is almost insoluble in warm water, but readily dissolves in alcohol or in aqueous alkalis; from the former solution, it is re precipitated by water, and from the latter by acids. On evaporating the filtrate from the phlobaphen, an odour of charred sugar was noticed, this result suggesting the presence of a glucoside.

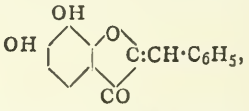
The freshly-prepared extract, when treated with lead acetate, yielded a yellow precipitate of a lead salt which, when suspended in water and decomposed by hydrogen sulphide, furnished a yellow solution, from which a yellow gum was obtained by evaporation. This product, when dissolved in water and extracted with ether, gave a light yellow ethereal solution, from which a semi-fibrous, yellow mass separated. This substance was soluble in hot water, alcohol, or acetic acid, and separated from the last-mentioned solvent in small, lemon-yellow crystals, which gave the reactions of fisetin (compare Perkin and Hummel, *Journ. Soc. Chem. Ind.*, 1895, 459, and Hummel and Cavallo, *Proc.*, 1894, x., 11). At the time this work was carried out, the author had no access to the original papers of the foregoing authors.

After separating the ethereal extract, the aqueous solution was hydrolysed by boiling with dilute hydrochloric acid; this reaction led to the precipitation of phlobaphen, several fractions of the product being collected during evaporation.

These fractions, which are probably different anhydrides of the same tannin, were all readily soluble in alcohol or aqueous alkalis, giving rise to deep reddish-brown solutions; they readily reacted with bromine, evolving hydrogen bromide and giving an amorphous powder lighter in colour than the original substance; this product yielded traces of methyl bromide on treatment with sodium hydroxide solution. Phloroglucinol and protocatechuic acid were obtained from the phlobaphen by fusion with potassium hydroxide.

69. "*Butein.*" (A preliminary notice). By (the late) J. J. HUMMEL and A. G. PERKIN.

The announcement (*Proc.*, vol. xix, p. 126) that a paper by E. G. Hill on "The Coloured Constituents of *Butea frondosa*" would be read at the next meeting of the Society, renders necessary the following note on the investigation of this dyestuff, which is now proceeding. *Butein*, the colouring matter of the flowers of *B. frondosa* (Hummel and Cavallo, *Proc.*, 1894, x., 11), $C_{15}H_{10}O_5$, probably exists in two modifications:—(*a*) Colourless (C = 66·62; H = 4·32), and (*b*) orange-yellow (C = 66·31; H = 4·19), which, on fusion with alkali, give resorcinol and protocatechuic acid. The *tribenzoyl* derivative, $C_{15}H_7O_5(C_7H_5O)_3$ (C = 74·02; H = 4·05), which forms colourless needles (m. p. 155—157°), and the *triacetyl* compound, $C_{15}H_7O_5(C_2H_3O)_3$ (C = 63·50; H = 4·05) have been studied. The dyeing properties of butein very closely resemble those of benzylideneanhydroglycogallol (Friedländer and Rudt, *Ber.*, 1896, xxix., 879),—



the compound being probably a member of this or some closely allied series. When it is heated with sulphuric acid, a colouring matter is produced, the tinctorial properties of which are somewhat similar to those of alizarin.

70. "*The Relative Affinities of Polybasic Acids.*" By H. M. DAWSON.

The conceptions of avidity, as defined originally by Thomsen, and of affinity, as based on the theory of electrolytic dissociation, are not always identical.

For weak polybasic acids, the relative affinities are determined essentially at all ordinary concentrations by the primary dissociation of a single hydrogen ion, and direct values for the affinities as measured by their base combining powers will be obtained if the quantities of the two acids competing for a base are in the ratio of their molecular and not their equivalent weights.

In the case of strong polybasic acids, the affinity is a complex factor determined by more than one dissociation phenomenon, and a method of viewing such partition phenomena in the case of the stronger polybasic acids is brought forward.

71. "*The Chemical Dynamics of the Reactions between Chlorine and Benzene under the Influence of Different Catalytic Agents and of Light.*" By A. SLATOR.

With a large excess of benzene, the reactions between this hydrocarbon and chlorine are practically limited to the two changes represented by the following equations: $C_6H_6+Cl_2=C_6H_5Cl+HCl$, $C_6H_6+3Cl_2=C_6H_6Cl_6$, the relative amounts of the two chief products depending on the conditions of the experiment.

The velocity of these reactions has been measured under various conditions, especially under the influence of different catalytic agents. A chlorine solution of suitable concentration in dry benzene being employed, the velocity of the reactions is measured by simultaneous titrations of chlorine and hydrogen chloride.

The reaction velocity without a catalytic agent is too small to be measured. Under the influence of iodine chloride, both the substitution and addition reactions take place. The velocity of disappearance of free chlorine is found to be proportional to the chlorine concentration and to the square of the iodine chloride concentration; the

temperature coefficient of the reaction is very small. By investigating the reaction in carbon tetrachloride solution with varying quantities of benzene, it was shown that the velocity is proportional to the concentration of the hydrocarbon. It is found by estimating the hydrogen chloride that 70 per cent of the chlorine takes part in the substitution reaction, whilst the remainder combines additively.

This ratio remains constant, even when the solvent is changed, or the concentration of chlorine, iodine chloride, or benzene varied; it is also only slightly affected by temperature.

With tin tetrachloride and with ferric chloride as catalytic agents, the substitution reaction alone takes place. The accelerating effect due to a mixture of iodine chloride and tin tetrachloride is found to be approximately equal to the sum of that due to each agent acting separately.

Under the influence of light without catalytic agents, the addition reaction alone occurs; under conditions of equal illumination, the velocity of this change is found to be proportional to the square of the chlorine concentration.

72. "*The Diazo-reaction in the Diphenyl Series.* Part I. *On Dianisidine and* 3 : 3'-*Dichlorobenzidine.*" By J. C. Cain.

On heating aqueous solutions of the diazonium salts prepared from dianisidine and 3 : 3'-dichlorobenzidine, dark coloured, insoluble, infusible compounds are obtained instead of the expected dihydroxy-derivatives.

The products, which appear to be quinones, agree in composition with the formulæ, $O{:}C_6H_3(OMe){:}C_6H_3(OMe){:}O$ or

$$\begin{matrix} C_6H_3(OMe)\cdot O \\ | \qquad\quad | \\ C_6H_3(OMe)\cdot O \end{matrix},$$

and—

$$O{=}\!\!<\!\!{}^{C_6H_3Cl{:}C_6H_3Cl{:}O}_{C_6H_3Cl{:}C_6H_3Cl{:}O}, \quad \text{or} \quad O\!<\!\!{}^{C_6H_3Cl\cdot C_6H_3Cl\cdot O}_{C_6H_3Cl\cdot C_6H_3Cl\cdot O}\!>\!O,$$

the former in each case being the more probable one.

These substances are not affected by the usual reducing agents, but form additive compounds with hydriodic acid and acetic anhydride which are easily decomposed by alkalis, the original compounds being regenerated.

A strong aqueous solution of the diazonium salt from dichlorobenzidine, when heated with twice its volume of concentrated sulphuric acid, yields a very small quantity of 4 ; 4'-dihydroxy-3 : 3'-dichlorodiphenyl (m. p. 124°); dianisidine does not give rise to a similar product.

PHYSICAL SOCIETY.

Ordinary Meeting, May 8th, 1903.

Dr. R. T. Glazebrook, F.R.S., President, in the Chair.

Mr. T. H. Blakesley exhibited and described a Spectroscope of Direct Vision, of one kind of glass, and of minimum deviation for every ray that comes into the centre of the field of view.

The refracting angles are such that the cosines of half the refracting angles are equal to half the index of refraction for the ray which is to have no deviation. The first prism is right-angled, and has one angle equal to the refracting angle calculated by the above rule. The second prism and the third possess the refracting angle so obtained, and the fourth is similar to the first. The first and fourth prisms produce the minimum deviation for the selected ray, and operate as reflectors as well. Thus the second prism can be so arranged as to increase the dispersion, but to neutralise the deviation. At this point the ray will be parallel to the incident light but not collinear with it. The third and fourth prisms bring the ray back to collinearity with the incident ray, and each adds its proper dispersion. The first and second are rigidly connected, as are the third and fourth; but these two parts rotate relatively to each other about the symmetrical point, so as to bring any portion of the spectrum into the field of the telescope, which is rigidly connected with the second part, as is the collimator with the first part. The glass selected is heavy and highly dispersive, and the total disperson between the lines A and G is over 18°. The plan adopted can be extended by employing more than one of the arrangements described, in sequence. Mr. Blakesley showed several photographs of the solar spectrum taken with the instrument, and exhibited the iron spectrum to the Fellows present.

Prof. S. P. Thompson congratulated the author upon the design of the instrument and the ingenious principle involved.

Prof. J. D. Everett said that in all previous direct-vision spectroscopes half the prisms increased the dispersion and the other half diminished it; whereas in this instrument all the prisms combined to increase it. He regarded the arrangement as a triumph of inventive skill.

The Chairman said he agreed with the remarks of Prof. Thompson and Prof. Everett. He had had an opportunity of examining the instrument at the National Physical Laboratory, and found the dispersion large and the definition good.

Prof. J. D. Everett read a paper "*On the Mathematics of Bees' Cells.*"

A single cell open at one end has nine faces, three of them rhombuses meeting in a point, and the other six the faces of a hexagonal prism. The pointed ends of one layer of cells fit in between those of an opposite layer, and each rhombus belongs equally to both. The centres of all the rhombuses lie in one plane. If h denote the distance of the plane of either set of apexes from this medial plane, and s the side of a hexagon, the edge of a rhombus is $\sqrt{s^2+h^2}$, the longer diagonal $s\sqrt{3}$, and the shorter $\sqrt{s^2+4h^2}$. The cosines of the angles of a rhombus are $\pm(s^2-2h^2)/(2s^2+2h^2)$, and the cosines of the angles which the line bounding a prism face makes with the prism edges are $\pm s/\sqrt{s^2+h^2}$. Comparing the areas with what they would be if the ends were flat, each rhombus is greater by $\frac{1}{2}\sqrt{3}s\{\sqrt{(s^2+4h^2)}-s\}$, and each prism face is less by $\frac{1}{2}sh$. If the number of cells were infinite, the number of prism walls would be double the number of rhombuses. It may be taken as double. Then, for the greatest economy of material, if a rhombus is n times as thick as a prism wall, we must have $h-\frac{1}{2}n\sqrt{3}\sqrt{s^2+4h^2}$ a maximum, for constant s. This gives $s^2=(12n^2-4)h^2$, leading to $(s^2-2h^2)/2(s^2+h^2)=(2n^2-1)/(4n^2-1)$, $s/\sqrt{s^2+h^2}=1/\sqrt{3(4n^2-1)}$. The usual assumption $n=1$ gives $\pm\frac{1}{3}$ for both these expressions. The average value of n from observations may be taken as $\frac{8}{5}$, giving $\pm\frac{7}{15}$ and $\pm\sqrt{\frac{1}{2\frac{1}{4}}}$ as the values of the cosines. The values $\pm\frac{1}{3}$ for the cosines give what is regarded as the normal type of the bee's cell. The faces of a cell are perpendicular to the six edges of a regular tetrahedron, and the edges of the cell to the faces of the tetrahedron.

Prof. S. P. Thompson said he could not agree with the author that the bees for a given volume of cell wanted to use a minimum of material. He thought the amount of wax necessary was determined by other considerations.

Prof. Everett said he thought the bees were guided by simplicity of construction. If we suppose the bees in the two layers of cells to be arranged like two tiers of cannon balls in the most compact piling, the centres of the bees coinciding with the centres of the balls, each bee takes part in the building of walls between itself and its nearest neighbours, each wall being midway between the two bees, and at right angles to the line joining them. According to the best authorities, there was much irregularity in the construction of bees' cells, but the received form (described in the paper) was a fair average.

Mr. W. A. Price read a note on "*The Coloured Map Problem.*"

He referred to the fact that only four colours are

required to colour a map on the surface of a simply connected region, such as a sphere, in such a way that two countries marching on a boundary line are coloured differently, and exhibited two models of anchor rings the surfaces of which were divided in each case into six sections, each of which marched with the other five; and a model of a ring having a cross-bar or stud, the surface of which was divided into eight sections each of which marched with the other seven. In the case of maps on such surfaces, at least six and eight colours would be required in the respective cases.

Prof. EVERETT said that a proof of the ordinary rule for the number of colours required had been attempted by Prof. Tait in a paper to the Edinburgh Royal Society.

Dr. WATSON read a "*Note on the Construction and Attachment of Galvanometer Mirrors.*"

It has often been pointed out, notably by Lord Rayleigh and Prof. Threlfall, that it is better to increase the sensitiveness of galvanometers and similar instruments by improving the optical system, rather than by pushing the electrical sensitiveness to extreme limits. When working with ordinary silver on glass mirrors difficulties arise in connection with the attachment of the fibre and the fact that it is necessary to use a varnish, which in all cases produces distortion. These difficulties have been overcome by using quartz instead of glass, and platinum instead of silver. A disc of quartz, the diameter of the mirror required, and about 1 m.m. thick, is cut from a rod of the fused material. A small tag of quartz rod is then fused to the edge. This is for the attachment of the fibre. One surface of the disc is then polished and coated with a platinising solution. The whole is then put into a muffle-furnace and raised to a red heat, when platinum is deposited upon the surface. The disc can then be ground down in thickness from behind until it is as thin as required. This does not produce distortion of the mirror, because of the unstrained condition of the fused quartz. Half-silvered mirrors can be obtained by adjusting the thickness of the coating of the platinising solution. Dr. Watson exhibited several galvanometer mirrors and also larger mirrors on plate glass and lenses.

Mr. C. V. BOYS congratulated the author upon a valuable and interesting paper. The subject of mirrors was one which for many years had troubled and perplexed experimenters. It was surprising that a new method of making mirrors, such as that described in the paper, could have so many advantages over the usual processes.

Mr. J. W. SWAN expressed his interest in the paper, and said he was glad to see that the seed sown by Mr. Boys in the employment of fused quartz was being cultivated to-day. The paper was a valuable practicable contribution. He asked for the composition of the platinising solution.

The CHAIRMAN, in congratulating the author, said he had had an opportunity of discussing with Dr. Watson the uses to which these mirrors might be put, and he had seen their many advantages in a vertical-force magnetograph at the National Physical Laboratory.

Dr. Watson said he thought the composition of the solution was a secret, but it was a comparatively inexpensive liquid, obtainable from Messrs. Johnson and Matthey.

CORRESPONDENCE.

THE ACCURACY OF QUANTITATIVE ANALYSIS.

To the Editor of the Chemical News.

SIR,—It is important that the student of quantitative chemical analysis should get a grasp of the different sources of error which affect his work, and also of the (total) error to be expected in the final result.

On classifying the various errors and considering their magnitudes, we find that most of them may be made, at will, as small as we please, *e.g.*, errors in graduated vessels, errors in calculation, &c.

The errors not within our control are unavoidable errors of manipulation, *e.g.*, errors introduced by weighing (even with correct weights), errors in reading burettes, &c.; the magnitude of these will not, as a rule, be more than one or two parts in a thousand; *i.e.*, the total amount of substance taken as calculated from the results of analysis is too small or too large by one or two parts per thousand, or 0·1—0·2 per cent of the amount really taken.

(It is much preferable to state an error in this way to discussing the error on the percentage of an element in a compound as found by a determination).

This error then of 1—2 parts in a thousand is the only considerable one, and it would seem possible to obtain analyses correct to this limit in gravimetric and also in volumetric analysis. In some cases this accuracy is obtained, but it is doubtful whether, for the ordinary student, such accuracy should be expected or insisted on. Very various views appear to be current among teachers of chemistry with regard to the degree of accuracy it is desirable to demand from the student for a satisfactory analysis, but I think most chemists will agree that it is a matter of some importance.

There are always special considerations in every particular analysis, but, for the average straightforward determination, perhaps we may put the maximum permissible error on the work as about one part in a hundred. It would be of interest to have the views of your readers on this subject, and to learn what the practice is in the various institutions for the instruction of practical chemistry.—I am, &c.,

CHARLES E. FAWSITT.

University of Edinburgh,
May 9th, 1903.

SLIPSHOD METHODS OF OIL AND PAINT ANALYSIS.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS of May 8th (vol. lxxxvii., p. 217), Mr. J. G. McIntosh takes exception to the recording of the constants of oils, and the method of expressing acid determinations, &c. Although the number of determinations of these "oil-constants" is very great, your correspondent surely goes too far in saying that the data are of "no value whatever except in regard to the particular sample operated on." On the contrary, almost the whole of our knowledge of the chemical and physical characteristics of the various oils, and their similarities and differences, has been obtained by the careful determination of these "constants" on samples of known origin. The analyst necessarily relies largely upon such constants when he reports upon an oil submitted to him for examination.

The figures given in Allen's "Commercial Organic Analysis" are, unless otherwise stated, evidently the collated results of the experience of many observers. The great majority of the readers of Allen's work undoubtedly understand them in this way. Mr. McIntosh admits that two oils of the same nature vary to some extent as regards their characters, and it is the recognition of this fact which gives rise to the recording of—to use a Hibernicism—these variable constants. Assuming the practical work to be properly carried out, there is nothing so valuable as a record of the natural variations to which oils and other natural products are liable. Mr. McIntosh says that there must be a cause for any variation in the composition of various specimens of oils of the same nature, and he adds that "efforts should rather be made to discover the cause of the variation than to register the results . . . ." But is it not a fact that the chief causes of the variations are natural and inherent, being due to differences in the proportions of the proximate constituents, which cannot be either remedied or controlled? Cows' milk is a natural product which varies in composition to a certain, more or

less known, extent, and hundreds of thousands of analyses of milk are on record showing the natural variations of this product; but Mr. McIntosh appears to contend that analysts should neglect the compiling of tables showing the limits of natural variation of milk, and regards them as valueless; apparently arguing that if a specimen of milk is not of strictly normal composition it ought to be, and therefore that its existence should be ignored.

The method of expressing the acidity of a product in terms of so much alkali absorbed has much to recommend it. In many cases it is impossible to record this acidity in terms of the acid present, since the composition, basicity, &c., of the latter are often unknown. Hence the use of the term "acid value" or "acid number," which expresses in a convenient form the amount of caustic potash required to neutralise the acid, namely, the number of milligrammes of KOH for every 1 grm. of the substance under examination. In the case of the Reichert process so generally used for the examination of butter and margarine, it is difficult to see what better method of expressing the results could be devised. The process is an arbitrary one, and the volume of decinormal alkali (not necessarily potash) required for the neutralisation of the volatile acids has to be observed. If from this result the volatile acids are calculated in terms of *butyric acid*, we obtain a figure which may be very easily confused with that for the "soluble acids" of butter, and on this ground alone any such alteration would be disadvantageous.—I am, &c.,

ARNOLD R. TANKARD.

67, Surrey Street, Sheffield.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 16, April 20, 1903.

Specific Heat and Heat of Volatilisation or Fusion of Aniline and certain other Organic Compounds.—M. de Forcrand.—The author re-determines the specific heat and heat of volatilisation or fusion of a number of organic compounds whose thermo-chemical constants are not very definite. This set of researches has in view the verification of the general relation $\frac{L+S}{T} = 30$ (varying from 28 to 32). For aniline the following numbers are found:—

Specific heat in the liquid state = 0·4838 at 0°
Specific heat in the solid state = 0·2230 at −15°
Heat of solidification .. .. = 0·0399 cal. at −7·03°
Molecular heat of solidification = 3·711 cal. at −7·03°

The same observations are also made with nitrobenzene, benzene, and acetic acid.

Sulphur Waters from the Bayen Spring at Bagnères-de-Luchon.—F. Garrigou.—The author makes the following observations as a result of his experiments on the sulphur waters obtained from the Bayen Spring at Bagnères-de-Luchon:—(1) Sulphuretted hydrogen escapes in abundance from the water, because it exists either in the free state or combined in the form of sulphohydrates. (2) After the expulsion of this acid only minute quantities of gas are evolved, proving the very slow decomposition of the remaining monosulphide. (3) By the addition of aluminium sulphate to the remaining water at boiling-point, a rapid evolution of a further quantity of sulphuretted hydrogen takes place, on account of the monosulphide being decomposed into hydrogen sulphide with formation of alumina.

Soluble Cellulose.—Léo Vignon.—By acting on oxycellulose in the cold, aqueous solutions of potash cause the production of a soluble cellulose, which can be precipitated by hydrochloric acid and the chlorides of the alkalis and alkaline earths.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, May 26th, at 5 o'clock, Prof. Edmund J. Garwood delivers the first of two lectures at the Royal Institution on "The Work of Ice as a Geological Agent"; on Thursday, May 28th, at the same hour, Prof. J. A. Fleming commences a course of two lectures on "Electric Resonance and Wireless Telegraphy"; and on Saturday, May 30th, at 3 o'clock, Prof. S. P. Thompson begins a course of two lectures on "The 'De Magnete' and its Author." The Friday Evening Discourse on May 29th will be delivered by His Highness the Prince of Monaco, on "The Progress of Oceanography"; and on June 5th by Prof. H. H. Turner on "The New Star in Gemini." The Extra Discourse on June 19th will be delivered in French by Prof. Pierre Curie on "Radium."

Contributions to Our Knowledge of Cuprous Compounds.—G. Bodlaender and O. Storbeck.—Cuprous chloride, on contact with water, undergoes a decomposition which gives rise on the one hand to hydrochloric acid and suboxide of copper, and on the other hand especially to cupric chloride, with a deposition of metallic copper. This decomposition is retarded by the successive addition of chlorides; a solution containing more than 0·05 molecule of KCl per litre dissolves cuprous chloride without decomposition. In aqueous solution, cuprous chloride is decomposed partially in the form of complex ions. Solutions of chloride of potassium containing 0·05 to 0·4 molecule of the salt per litre dissolve cuprous chloride, with the formation of the compound $CuCl_2K$, while with more concentrated solutions the formula of the complex salt is $CuCl_3K_2$. The molecule of the complex cuprous salts contains certainly only one atom of copper, but the authors have not yet been able to determine definitely whether the cuprous ions were mono- or di-atomic. During the course of their research, the authors have determined a few solubilities. The solubility of cuprous chloride in pure water = 2·851 millimolecules of Cu per litre at about 20°; the solubility in a concentrated solution of KCl, at about 16—20°, is as follows:—One litre of solution of KCl at 0·05, 0·01, 0·2, 1·0, and 2·0 grm.-molecules dissolve 0·002411, 0·004702, 0·009458, 0·0970, and 0·3840 grm.-atoms of copper. *Solubility in* SO_4Cu.—The total quantity of copper which passes into solution is as follows, in grm.-millimolecules per litre:—

Concentration in SO_4Cu ..	0·49375	1·4812	2·4687	2·9625	5·9375
Total copper .	3·125	3·915	4·786	5·193	7·276

In any case, the quantity of copper dissolved in the state of cuprous chloride varies in an irregular fashion as the proportion of cupric sulphate present increases.—*Zeit. Anorg. Ch.*, vol. xxxi., p. 1.

MEETINGS FOR THE WEEK.

MONDAY 25th.—Society of Chemical Industry, 8. "Neatsfoot Oil" and "The Nitric Acid Test for Cotton-seed Oil," by J. H. Coste, F.I.C., and E. T. Shelbourn, F.I.C.

TUESDAY, 26th.—Royal Institution, 5. "The Work of Ice as a Geological Agent," by Prof. Edmund J. Garwood, M.A.

THURSDAY, 28th.—Royal Institution, 5. "Electric Resonance and Wireless Telegraphy," by Prof. J. A. Fleming, F.R.S., &c.

FRIDAY, 29th.—Royal Institution, 9. "The Progress of Oceanography," by His Serene Highness Albert, Prince of Monaco.

SATURDAY, 30th.—Royal Institution, 3. "The 'De Magnete' and its Author," by Prof. S. P. Thompson, F.R.S.

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THE CHEMICAL NEWS.

Vol. LXXXVII., No. 2270.

A NEW CLASS OF ORGANO-TIN COMPOUNDS CONTAINING HALOGENS.*

By WILLIAM J. POPE, F.R.S.,
Professor of Chemistry, Municipal School, Manchester,
and
STANLEY J. PEACHEY.

Most of the organo-tin compounds which have hitherto been described may be regarded as derived from the hypothetical stannimethane, SnH_4, and, adopting a nomenclature based upon the name of this substance, the simple types of known organo-tin compounds may be described as the tetralkylstannimethanes, the trialkylstannimethyl chlorides, bromides, and iodides, and the dialkylstannimethylene chlorides, bromides, and iodides. The analogy between the various classes of derivatives of stannimethane and of methane is as yet incomplete in that no organo-tin compounds corresponding in constitution to chloroform, bromoform, and iodoform have been described; methods for preparing such derivatives are, however, given in the present paper, so that the analogy of constitution existing between the corresponding classes of alkyl and halogen compounds of carbon and tin is shown to be complete, and of the kind illustrated by the following table:—

$C(CH_3)_4$	Tetramethylmethane.
$C(CH_3)_3I$	Trimethylmethyl iodide.
$C(CH_3)_2I_2$	Dimethylmethylene iodide.
$C(CH_3)I_3$	Methyliodoform.
CI_4	Carbon tetriodide.
$CH_3.CO.OH$	Acetic acid.
$Sn(CH_3)_4$	Tetramethylstannimethylmethane.
$Sn(CH_3)_3I$	Trimethylstannimethyl iodide.
$Sn(CH_3)_2I_2$	Dimethylstannimethylene iodide.
$Sn(CH_3)I_3$	Methylstanniodoform.
SnI_4..	Stannic iodide.
$CH_3.SnO.OH$ ..	Methylstannoxylic acid.

Methylstanniodoform, $CH_3.SnI_3$.

Since tetramethylstannimethane is acted upon by iodine with production of trimethylstannimethyl iodide and methyl iodide, in accordance with the following equation:—

$$Sn(CH_3)_4 + I_2 = Sn(CH_3)_3I + CH_3I,$$

it seemed not unlikely that, on replacing the iodine by stannic iodide, the reaction would take the course indicated by the following equation:—

$$Sn(CH_3)_4 + SnI_4 = Sn(CH_3)_3I + Sn(CH_3)I_3.$$

This was found to be the case.

On warming a mixture of tetramethylstannimethane (two parts) and stannic iodide (seven parts) on the water bath, the iodide rapidly dissolves, and, after a few hours' standing at the ordinary temperature, methylstanniodoform crystallises in large straw-coloured prisms; the separation of the latter is rendered more complete by the addition of petroleum ether, and, after filtration, the stanniodoform derivative is purified by crystallisation from ether or light petroleum. It crystallises in long needles or prisms closely resembling iodoform in colour, and melts at 82—84°; it gradually volatilises at 100° and, when slowly heated, distils without decomposition. It is odourless and dissolves very readily in alcohol, acetone, and benzene. The following analytical results were obtained:—

0·3083 gave 0·0254 CO_2 and 0·0172 H_2O. C = 2·24, H = 0·62.

0·2964 required 17·5 × 0·0169 $AgNO_3$ for titration. I = 74·4.

Theory for $Sn(CH_3)I_3$:—C = 2·33, H = 0·58, I = 74·0.

Methylstannoxylic Acid, $CH_3.SnO.OH$.

Methylstanniodoform is insoluble in cold water, but dissolves in boiling water, giving a solution from which the iodoform derivative cannot subsequently be crystallised; as this behaviour should be attributable to the occurrence of hydrolysis in the following sense, $CH_3.SnI_3 + 3H_2O = CH_3.Sn(OH)_3 + 3HI$, methylstanniodoform was evaporated on the water-bath with an aqueous solution of three molecular proportions of soda; as evaporation proceeded, a white precipitate of methylstannoxylic acid was deposited, the reaction being represented by the following equation:—

$$CH_3.SnI_3 + 3NaHO = CH_3.SnO.OH + 3NaI + H_2O.$$

After washing with water, solution in acetic acid, and precipitation with ammonia, the substance gave the following analytical results:—

0·3887 gave 0·0990 CO_2 and 0·0822 H_2O and 0·3532 SnO_2 C = 6·94, H = 2·36, Sn = 71·60.

0·3396 gave 0·0869 CO_2, 0·0800 H_2O, and 0·3024 SnO_2. C = 6·97, H = 2·63, Sn = 70·16.

$CH_3.SnOOH$ requires C = 7·18, H = 2·41, Sn = 71·24.

By the action of methyl iodide on sodium stannite, G. Meyer (*Berichte*, vol. xvi., p. 1439) obtained a white powder in which he made one determination of tin, and which he considered to be probably the acid which we now describe. On repeating Meyer's preparation we found that the substance obtained is identical with the methylstannoxylic acid prepared from methylstanniodoform. To the very scanty description given by Meyer we would add the following.

The acid is conveniently prepared by dissolving stannous chloride (100 grms.) in the minimum quantity of water, and adding concentrated caustic soda solution until the precipitate formed at first just re-dissolves. To the solution thus obtained (300 c.c.), absolute alcohol (200 c.c.) and methyl iodide (90 grms.) are added; the liquid becomes warm and, after two days' repose at the ordinary temperature, is saturated with carbon dioxide, filtered, and evaporated on the water-bath. During the evaporation, methylstannoxylic acid separates in white crystalline crusts, and is obtained in a practically pure condition after filtration and washing with boiling water. The acid is insoluble in water and the ordinary organic solvents, but dissolves slowly in boiling acetic and formic acids. On adding ammonia to the acetic acid solution after dilution with water, no precipitate forms, but on boiling, methylstannoxylic acid separates in a state of purity; the fact that no precipitate occurs until the solution is boiled, indicates the existence in solution of an ortho-acid, $CH_3.Sn(OH)_3$, which is only decomposed on heating. Methylstannoxylic acid decomposes slowly at 120—130°, but no volatile tin compound is evolved; on rapid heating it chars, and, when ignited, smoulders, leaving a residue of stannic oxide. On boiling the acid with dilute caustic potash the greater part dissolves, but the solution never becomes quite clear; when the acid is boiled with stronger potash solution, a rapid evolution of methane occurs, a sublimate of trimethylstannicarbinol, $(CH_3)_3Sn.OH$, forms, and the solution is afterwards found to contain dimethylstannimethylene oxide, $(CH_3)_2SnO$. Lastly, on mixing the acid with solid potash and heating, after the addition of a small quantity of water, methane containing a considerable proportion of tetramethylstannimethane is given off; the latter substance was identified by freezing it out of the gas and determining its boiling-point and behaviour towards iodine. The

* From the Chemical Laboratories, Municipal School of Technology, Manchester. Read before the Royal Society, May 14, 1903.

fact that methylstannoxylic acid is not wholly soluble in dilute potash is attributable to a part of it being decomposed with evolution of methane and production of stannic oxide which remains undissolved by the potash. The evolution of methane which attends the heating of methylstannoxylic acid with potash, is quite analogous to the decomposition which occurs when sodium acetate is heated with soda-lime, whilst the formation of dimethylstannimethylene oxide is analogous to the production of acetone by heating calcium acetate; it is, however, difficult to find analogies for the formation of trimethylstannimethyl alcohol and tetramethylstannimethane during the heating of the stannoxylic acid with potash. The four kinds of change would seem to take place in accordance with the following equations:—

1. $CH_3.SnO.OH = CH_4 + SnO_2$.
2. $2CH_3.SnO.OH = (CH_3)_2SnO + SnO_2 + H_2O$.
3. $3CH_3.SnO.OH = (CH_3)_3Sn(OH) + 2SnO_2 + H_2O$.
4. $4CH_3.SnO.OH = (CH_3)_4Sn + 3SnO_2 + 2H_2O$.

Equation 2 is similar to that suggested by Pfeiffer (*Berichte*, vol. xxxv., p. 3303), in order to explain the fact that he obtained diethylstannimethylene oxide instead of ethylstannoxylic acid by the action of ethyl iodide on sodium stannate.

A number of attempts were made to prepare salts of methylstannoxylic acid, but these have been uniformly unsuccessful owing to the very feebly marked acidic characters of the substance. The acidic properties of methylstannoxylic acid are, in fact, so very slight that the substance tends to react in the ortho-form rather than in the stannoxylic condition, although the reverse is true in the case of carboxylic acids. Thus, on treating methylstannoxylic acid with concentrated hydriodic acid, it is immediately converted into methylstanniodoform, so that the reaction, by means of which we first prepared the acid, is a reversible one; since methylstannoxylic acid is very easily prepared in quantity by the action of methyl iodide on alcoholic sodium stannite solution, the most convenient method of preparing the stanniodoform derivative consists in treating methylstannoxylic acid with strong hydriodic acid, and, after filtration, crystallising the product from a mixture of benzene and light petroleum.

Methylstannibromoform, $CH_3.SnBr_3$.

Methylstannoxylic acid dissolves readily in concentrated hydrobromic acid, and on extracting the solution with light petroleum and evaporating the solvent, methylstannibromoform separates. After crystallisation from petroleum it is obtained in the form of long colourless prisms which melt at 50—55° and may be distilled without decomposing. The substance fumes slightly in the air and dissolves to a clear solution in water. Methylstannibromoform is readily soluble in the ordinary organic solvents. The following analytical results were obtained:—

0·4664 gave 0·0563 CO_2 and 0·0382 H_2O. C = 3·29, H = 0·91.

$CH_3.SnBr_3$ requires C = 3·21 and H = 0 80.

Methylstannichloroform, $CH_3.SnCl_3$.

Methylstannoxylic acid dissolves in concentrated hydrochloric acid with evolution of heat, and, after saturating the solution with anhydrous calcium chloride and extracting with benzene, the benzene solution yields a residue when evaporated which slowly crystallises in the desiccator. On gently warming methylstannoxylic acid in a current of dry hydrogen chloride, reaction occurs and methylstannichloroform distils, condensing in the receiver as a colourless crystalline material. The same product is formed on treating the acid with phosphorus trichloride. Methylstannichloroform crystallises from light petroleum in long colourless prisms melting at 105—107° and distils without decomposition at 179—180°. It fumes in the air, dissolves to a clear solution in water, and is very soluble in the ordinary organic solvents.

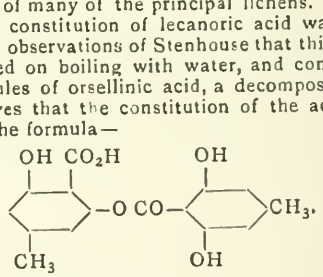
THE CHEMICAL RESEARCHES OF EDWARD SCHUNCK, D.Sc., PH.D., F.R.S.*

By W. H. PERKIN, Junr., Ph.D., F.R.S.,
Professor of Organic Chemistry, Owens College, Manchester.

In endeavouring to give a brief survey of the work of Dr. Schunck, I should like to call attention to the opening sentences of a paper:—"On some of the Substances contained in the Lichens employed for the preparations of Archil and Cudbear." This important paper was read before the Chemical Society of London on January 4th, 1842, and is published in the first volume of the *Memoirs* of that Society. It begins thus:—"Our knowledge concerning that department of organic chemistry which embraces the colouring matters, and other principles nearly allied to them, is of the most imperfect kind. Though many other branches of organic chemistry have been so thoroughly and accurately investigated, that little or nothing remains to be known concerning them, this may be called an unexplored field." These words and many other statements in the same memoir are very interesting reading, as they show that at that early date the particular section of organic chemistry which deals with colouring matters had special attractions for Dr. Schunck. And indeed this investigation, which he states was commenced at Liebig's suggestion and in the celebrated Giessen laboratory, may be said to have had a fundamental influence on his life's work, because we find that nearly all of the investigations which he subsequently published deal with colouring matters, and especially with the colouring matters which occur in plants.

In the memoir just mentioned, Schunck succeeded in isolating from the lichens of the *Lecanora* and *Variolaria* section, which he was then investigating, a crystalline substance which he named *lecanorin*. Although accurate organic analysis was a matter of considerable difficulty in those days, he was nevertheless successful in correctly determining the composition of this important substance, and the formula $C_{16}H_{14}O_7 + 2H_2O$ which he gave to lecanorin has been repeatedly confirmed, and is the one in use at the present day.

Rochleder and Heldt, who soon afterwards (in 1843) obtained the same substance from *Evernia prunastri*, altered the name to *lecanoric acid* in order to indicate that it was an acid, and subsequently it was shown by Stenhouse, Hesse, and others, that Schunck's lecanorin is very widely distributed, and occurs as an important constituent of many of the principal lichens. A definite clue to the constitution of lecanoric acid was obtained through the observations of Stenhouse that this substance is hydrolysed on boiling with water, and converted into two molecules of orsellinic acid, a decomposition which clearly proves that the constitution of the acid is represented by the formula—



But the isolation of lecanorin was not the only important discovery which Schunck made in the course of his researches on the lichens. Heeren (in 1830) had made the observation that the lichens *Roccella tinctoria* and *Lecanora tartarea* (which were at that time, and indeed are now, largely used in the preparation of litmus and archil) contain a crystalline substance which he named *erythrin*, on account of its property of yielding a red colouring matter when its solution in ammonia is exposed to the air. He further observed that when boiled with alcohol it is converted into a different crystalline

* Read before the Manchester Literary and Philosophical Society, January 20, 1903. From the *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, xlvii., Part 3.

substance which does not show this colour reaction, and this he named *pseudoerythrin*. The determination of the nature of these substances was largely due to Schunck, who showed that his lecanorin (lecanoric acid), when boiled with alcohol, is very readily etherified, yielding a substance which is evidently identical with Heeren's pseudoerythrin; this latter substance is therefore, in all probability, the ethylic ester of lecanoric acid. When boiled with water, erythrin is decomposed into orsellinic acid and picroerythrin—a bitter substance which had already been obtained by Heeren—and, since this latter substance, on hydrolysis with lime water, is converted into orsellinic acid and erythrol, it follows that it is an ester derived from *one* molecule of orsellinic acid and *one* molecule of erythrol. The constitution of erythrin itself is thus shown to be that of an ester derived from *two* molecules of orsellinic acid and *one* molecule of erythrol.

The next subject to which Schunck turned his attention was the investigation of the colouring principles of the madder root (*Rubia tinctorum*), and in this field also he obtained remarkable and important results which at once attracted the attention of chemists. The madder root has been employed for dyeing purposes from very early times, but nothing was known as to the active principle contained in it until the year 1826, when Colin and Robiquet succeeded in isolating a colouring matter from it, and to this they gave the name *alizarin*. In 1828 Zenneck published a paper in which he made the remarkable suggestion that the alizarin was not contained in the madder root as such, but was present in combination with sugar or some similar substance. Schunck, in 1847, carefully investigated this matter, and was successful in isolating a bitter substance which he called *rubian*, and he showed that this substance, on boiling with dilute sulphuric acid, is decomposed with formation of alizarin and a sugar, and he was thus able to confirm Zenneck's suggestion.

A few years later (in 1851) Rochleder succeeded in obtaining this glucoside in a crystalline condition, and he then named it *ruberythrinic acid*. Græbe and Liebermann were the first to show that this crystalline ruberythrinic acid, when hydrolysed by boiling with dilute hydrochloric acid, yields, besides alizarin, glucose as the sugary constituent, and they represent the decomposition as taking place according to the equation—

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$

In 1876 Schunck discovered that when anthraquinone disulphonic acid is fused with soda, a new dihydroxyanthraquinone was formed, which he named *anthraflavic acid*. He subsequently isolated this same substance from the by products which had accumulated in the manufacture of artificial alizarin, and by fusing anthraflavic acid with potash he obtained a new and very interesting trihydroxyanthraquinone which he called *flavopurpurin*.

Schunck submitted both anthraflavic acid, and flavopurpurin to an exhaustive examination, and converted them into a number of beautifully crystalline derivatives, all of which he obtained in a state of great purity.

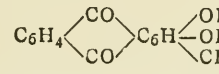
In the year 1876 Schunck associated himself with Roemer, and together they published an important series of papers on some of the di- and tri-hydroxyanthraquinones. They worked out a method for preparing pure purpurin or 1, 2, 4, trihydroxyanthraquinone, and devised an ingenious method for showing the presence of small quantities of alizarin in mixtures of this substance with purpurin. This consists in exposing the alkaline solution of the mixture to the air, when the purpurin is rapidly oxidised and destroyed. Any alizarin present remains unchanged, and can be readily detected by examining the absorption spectrum of the solution.

Schunck and Roemer were also the first to show that purpurin, when heated gradually to 300°, is converted, by a remarkable process of reduction, into chinizarin or 1, 4, dihydroxyanthraquinone.

At as recent a date as 1893 Schunck again took up the investigation of madder root, and in a paper published in conjunction with Marchlewski he describes the isolation of a new glucoside of the formula $C_{21}H_{20}O_9$, which he called *rubiadinglucoside*. This new glucoside crystallises in yellow needles, and is hydrolysed by dilute acids with formation of rubiadin and glucose—

$$C_{21}H_{20}O_9 + H_2O = C_{15}H_{10}O_4 + C_6H_{12}O_6.$$

The constitution of rubiadin was also carefully investigated, and it was found that this substance is a dihydroxymethylanthraquinone or methylpurpuroxanthin of the formula—



We may next notice the important researches which Schunck carried out on the nature of the constituents of the plants *Indigofera tinctoria*, *Isatis tinctoria*, and *Polygonum tinctorium*. All of these yield indigo when their leaves are macerated with water in contact with air, and the first-mentioned is grown in India and China in immense quantities, and serves as the source of nearly all the natural indigo which comes into the market.

It was known from very early times that indigo is not contained as such in the leaves of *Indigofera tinctoria*, and that, in order to produce indigo, it is necessary that the extract of the leaves shall undergo oxidation. In order to explain this, it was at first supposed that the leaves contained indigo white, and that this on oxidation was then converted into indigo. Schunck, however, showed that this could not be the case, because the clear aqueous extract of the leaves which deposits indigo on standing in the air is *acid*, and indigo white is only soluble in *alkaline* aqueous solutions. On investigating this matter, Schunck succeeded in 1853, in extracting from *Isatis tinctoria* an unstable syrupy glucoside which he named *indican*, and which, when warmed with dilute acids in contact with air, readily yielded indigo.

In 1900 Hoogewerff and H. ter Meulen succeeded in obtaining the glucoside in a crystalline condition, but Marchlewski and Radcliffe, in 1898, were the first to give a satisfactory explanation of the composition of this glucoside and its behaviour with acids.

There can be little doubt that Schunck's indican is, in reality, a glucoside of indoxyl, and that, on hydrolysis, it is first converted into glucose and indoxyl, and this latter in contact with air is at once oxidised to indigo. These changes may be represented thus:—

$$C_{14}H_{17}NO_6 + H_2O = C_6H_{12}O_6 + C_8H_7NO \text{ (indoxyl)},$$
$$2C_8H_7NO + O_2 = 2H_2O + C_{16}H_{10}N_2O_2 \text{ (indigo)}.$$

In connection with his researches on indigo, Schunck cultivated for some years the plant *Polygonum tinctorium* in his garden at Kersal, and a short time since he published a very interesting monograph entitled "The action of reagents on the leaves of *Polygonum tinctorium*." This monograph is illustrated with very beautiful coloured plates, which are designed to show the influence of various agents in bringing about the formation of indigo in the leaves of this plant.

During the last few years of his life Dr. Schunck devoted his energies to investigating the great problem of the nature of chlorophyll, the colouring matter which occurs in the green leaves of plants, and which plays such an all-important part in their development. Partly alone and partly in conjunction with Dr. Marchlewski, he published probably the most important papers which have appeared on this difficult subject. These papers contain the description of the best method yet devised for preparing chlorophyll, and there can be no doubt that this method, if it does not yield the pure colouring matter, certainly enables it to be prepared in a much purer condition than it was ever obtained before. In possession of this highly purified product, Schunck and Marchlewski submitted chlorophyll to a careful spectroscopical examination, and at the same time studied its chemical

properties, and made a most valuable investigation into the nature of the highly important products which are obtained when chlorophyll is submitted to the action of reagents. From the point of view of the future possibility of determining the actual constitution of chlorophyll, the experiments on the preparation of phylloxanthin, phyllocyanin, and the beautifully crystalline phyllotaonin, and the examination of their properties and mapping out of their absorption spectra, indicate that there is a possibility of acquiring a clear insight into the nature of the colouring matter at a not far distant date.

But probably the most far-reaching result which was obtained, certainly from a biological point of view, is the proof that *phylloporphyrin*—a crystalline substance which results from the action of alcoholic potash on phyllotaonin—is evidently closely allied to *hæmatoporphyrin*, a substance obtained from the hæmoglobin of the blood. Not only are the spectra of these two substances practically the same, but they also show similar chemical reactions.

It is probable that chlorophyll may play a similar part in the plant to that which hæmoglobin plays in the animal economy, and that its principal function is to convey carbunic acid to the plant in much the same way as hæmoglobin acts as a carrier of oxygen. The proof of the great similarity between chlorophyll and hæmoglobin must go far to break down any sharp line of demarcation which may, by some, still be thought to exist between the animal and vegetable kingdoms.

One thing is most noticeable in all the work which Dr. Schunck did, and that is the extreme care and accuracy with which all his experiments were carried out. The problems which he attempted to solve were among the most difficult in the whole range of organic chemistry, and his results were frequently called in question, but in nearly all cases it was subsequently found that his statements were correct. Anyone who has had the opportunity of examining his magnificent collection of the specimens of the substances he had discovered and investigated during the course of his many researches will, at once, realise the great trouble he always took to obtain everything in its purest possible form.

His work was always a labour of love, and his researches will always remain as models of what skill and perseverance can do in elucidating the most difficult of chemical problems. There can be no doubt that Science, and especially Organic Chemistry, has lost in Dr. Schunck an investigator of the front rank, whose place it will be very difficult to fill.

THE COMPOSITION OF INDIAN LATERITE.

By H. WARTH, D.Sc. (Tübingen),
and
F. J. WARTH, B.Sc. (Lond. and Birmingham).

After the appearance of Mr. T. H. Holland's paper on Laterite, in the *Geological Magazine* for February, 1903 (p. 59), we can at once give the results of our analysis of Indian laterite, without further introductory remarks. They are as follows:—

I.—*Pure Gibbsite from Kodikanal, previously recorded in the Mineralogical Magazine, May, 1902.*

H_2O	33·74
SiO_2	2·78
TiO_2	0·04
CaO	0·20
MgO	0·03
Fe_2O_3	0·44
Al_2O_3	62·80
	100·03

Molecules of water for one molecule of alumina = 3·06, which agrees very closely with the formula of gibbsite, $A_2O_3+3H_2O$. Specific gravity = 2·42.

II.—*Composition of four Bauxites very rich in Alumina, and containing little Iron, closely resembling the variety called "Wocheinite."*

	2. Kh.	3. Pl.	4. Sr.	5. Rw.
H_2O	26·47	24·00	28·10	26·94
SiO_2	0·93	1·79	2·01	2·35
TiO_2	1·04	3·30	6·49	6·61
CaO	0·36	0·04	0·45	0·15
MgO	—	0·02	—	nil
Fe_2O_3	4·09	6·21	5·48	6·53
Al_2O_3	67·88	64·64	58·23	57·50
	100·77	100·00	100·76	100·08
Molecules of water for one molecule of alumina	2·23	2·11	2·75	2·67

If we take the mean of these figures and calculate the proportion of gibbsite and diaspore ($Al_2O_3H_2O$) in the mixture, we find 72 per cent gibbsite and 28 per cent diaspore. As the proportions vary from 55 per cent to 88 per cent gibbsite, we may roughly say that these rich bauxites or "wocheinites" consist of about three-fourths gibbsite and one-fourth diaspore. Specific gavities:—No. 3 = 2·59; No. 5 = 2·39.

Average of Table III. equals 2·87, which implies 93·5 per cent gibbsite to 6·5 per cent diaspore, with variation from full gibbsite to 60 per cent gibbsite.

These bauxites in blocks and in powder are generally red with a shade of brown; No. 9 is light brown, Nos. 12 and 13 are of a deep red.

The specimens of Indian laterite given in Table IV. are arranged in order of their contents of free alumina, with the exception of the first, the pure gibbsite, which, however, is the richest in alumina if the water is eliminated. The specimens range from 68 per cent of free alumina down to nothing. There is thus every gradation in alumina from nearly theoretically strongest downwards, with no gap to speak of. If, however, we take into consideration the other constituents we find the specimens to fall into four distinct groups.

I. By itself stands the gibbsite from Kodikanal, which is so much free of foreign matter that in the ignited state it contains nearly 95 per cent of aluminium oxide. As stated in the notice in the *Mineralogical Magazine*, this mineral was found to form a deposit of one foot in thickness, consisting of loose crusts or plates which gave the impression of having been extracted from the underlying charnockite. The sp. gr. of this gibbsite was 2·42.

We next come to specimens of the far more extensive and thick-bedded surface deposits, which have hitherto all been classed under the name "laterite."

II. Of these laterites the first four specimens belong to our second group. They agree, as already stated, very well with those richest bauxites which have been given the separate name "wocheinite." They are characterised by their small amount of iron, and have even less silica than the recorded analysis of the celebrated original wocheinite, on an average 1·77 per cent compared with 6·29 per cent at Wochein. On the other hand, they contain much more titanium-dioxide. This large proportion of titanium-dioxide (maximum 6·61 per cent) is very characteristic of the rich bauxites, and a reference to the whole of the tables will show that the titanium-dioxide gradually decreases with the free alumina until there is only 0·01 per cent left. It remains a subject for further enquiry in what form the titanium exists when there is such a large proportion. From the fact of its dissolving when the entire mineral is treated with hot hydrochloric acid, and because there is always enough iron

III.—*Composition of Eight Specimens of Laterites in situ which are Bauxites.*

	6. Marwara.	7. Mahab.	8. Satara.	9. Nilgiris.	10. Nilgiris.	11. Pulsa.	12. Karad.	13. Satara.
H_2O	26·82	24·99	23·88	20·70	19·00	15·87	11·82	14·39
Quartz, SiO_2	—	—	—	—	10·52	—	1·77	—
SiO_2	3·90	0·72	0·37	3·14	0·23	3·56	4·20	0·90
TiO_2	0·38	0·42	4·45	—	0·10	0·13	0·10	1·59
CaO	0·35	0·00	0·86	—	0·40	0·52	nil	0·64
MgO	—	—	—	—	—	trace	trace	0·20
Fe_2O_3	13·75	23·41	26·61	37·88	34·37	47·27	51·25	56·01
Al_2O_3	54·80	50·46	43·83	38·28	35·38	32·65	30·86	26·27
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Molecules of water for one molecule of alumina	2·80	2·83	3·11	3·09	3·07	2·77	2·19	3·13

IV.—*Composition of Ten Detrital Laterites.*

Locality	14. Belgaum District.	15. Belgaum District.	16. Belgaum District.	17. Jabalpur.	18. Dharwar.	19. Balaghat.	20. Birbhum.	21. Madras neighbourhood.	22. Madras neighbourhood.	23. Madras neighbourhood.
Colour when pulverised	Lavender.	Red.	Brownish red.	Red.	Reddish brown.	Brown.	Reddish brown.	Reddish brown.	Brown.	Ochre.
H_2O	13·31	11·42	11·61	10·93	9·64	7·73	9·60	8·66	8·40	10·74
Free quartz, SiO_2	32·24	6·67	8·93	4·53	16·65	39·53	6·29	28·04	32·46	24·39
Combined SiO_2	9·94	13·35	16·69	23·32	14·79	7·96	17·49	14·07	13·33	10·42
TiO_2	0·04	0·25	0·10	0·43	0·02	0·01	0·04	0·01	0·01	0·01
CaO	0·00	nil	0·00	nil	0·04	—	0·03	nil	0·06	0·38
MgO	nil	nil	nil	nil	trace	—	nil	—	—	trace
Fe_2O_3	8·77	41·50	35·69	28·99	35·81	28·38	42·33	30·51	35·34	47·39
Al_2O_3	35·70	26·81	26·98	31·80	23·05	16·39	24·22	18·60	9·93	6·67
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	99·89	99·53	100·00
The same, with the clay calculated separately from the combined silica (kaolin = $Al_2Si_2O_7+2H_2O$).										
Free quartz, SiO_2	32·24	6·67	8·93	4·53	16·65	39·53	6·29	28·07	32·61	24·39
Clay as kaolin, $Al_2Si_2H_4O_9$	21·42	28·77	35·97	50·26	31·88	17·16	37·69	30·33	(27·39)	(20·22)
Balance identical with bauxite. H_2O	10·33	7·41	6·60	3·93	5·20	5·34	4·35	4·45	4·42	7·61
Balance identical with bauxite. TiO_2	0·04	0·25	0·10	0·43	0·02	0·01	0·04	0·01	0·01	0·01
Balance identical with bauxite. CaO	0·00	nil	0·00	nil	0·04	—	0·03	nil	0·06	0·38
Balance identical with bauxite. MgO	nil	nil	nil	nil	trace	—	nil	—	—	trace
Balance identical with bauxite. Fe_2O_3	8·77	41·50	35·69	28·99	35·81	28·38	42·33	30·55	35·51	47·39
Balance identical with bauxite. Al_2O_3	27·20	15·40	12·71	11·86	10·40	9·58	9·27	6·59	—	—
Total	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

present, we are inclined to believe that it exists chiefly as ilmenite. As already mentioned, the specimens of this group are mixtures of about three-fourths gibbsite and one-fourth diaspore (by weight). The mean specific gravity of two specimens was 2·49, which is more than that of the Kodikanal gibbsite. Our specimens have also the characteristic pisolitic structure, the globules varying from two to four millimetres in diameter.

III. The third group includes specimens such as geologists have hitherto called high-level laterites. They are bauxites which have formed from highly ferruginous igneous rocks. They belong mostly to the area of the Deccan trap, and we find that the proportion of ferric oxide in these bauxites is in close relation to the proportion of iron in the trap. In the same way the small proportion of iron in the preceding group of wocheinites indicates their origin from less ferruginous, probably gneissic rocks. A glance at the table, Group III., also shows the regularity with which the water decreases in the same order as the alumina, whilst the iron increases simultaneously.

Only in one case, that of No. 13, is there a slight departure from the rule. With the exception of two specimens containing quartz-sand, the quantity of silica is very small. Sample No. 7 contains only 1·14 per cent of substances other than the oxides of iron and aluminium besides water. The ferric oxide appears to be entirely or nearly entirely anhydrous. If this were not the case we should obtain a regularly increasing series for the molecules of water calculated from the total of the water for one molecule of alumina. Although the table shows that the figures vary, there is no great departure from the average, and, as already remarked, the mean of all the eight specimens implies anhydrous ferric oxide and a mixture of 93·5 per cent gibbsite and 6·5 per cent diaspore.

The identity of these high-level laterites with bauxite is also proved by comparison of their composition with that of other bauxites. Our No. 7 is almost identical with the bauxite from near Geissen with which Dr. Max Bauer compared the specimen from Mahé in the Seychelles.

Our specimen No. 9 comes very close to an Irish bauxite which has been analysed by Siemens, who found the following, according to Watts' "Dictionary of Chemistry":—

H_2O	21·5
SiO_2	3·5
TiO_2	2·0
Fe_2O_3	38·0
Al_2O_3	35·0
	100·0

Treated before the blowpipe, all the specimens of group No. III. are infusible, the general character of bauxite. Only in the case of No. 10 there were minute fused spots in small number, and No. 12 showed also traces of fusion, though they were doubtful. This behaviour of No. 10

and No. 12 is no doubt due to these specimens containing more silica than the others and free quartz-grains. This infusibility serves to distinguish the pure bauxities when mixed with Fe_2O_3 from the low-level laterites of the following group, No. IV., which (No. 14 excepted) fused unmistakably. Pure kaolins are also infusible, but if the material is distinctly red from iron the test holds good.

IV. The fourth group includes low-level laterites arranged in order of free alumina which calculation shows them to contain. The presence of free silica in the form of quartz is proved in all cases, and confirms a principal character of these deposits. Whenever distinct quartz-grains are seen in quantity, some of them being at times rather large, we may be sure that we have a detrital or low-level laterite. Besides the quartz-sand there is, however, generally an even larger proportion of clay (on the average 30 per cent of clay and 20 per cent of free quartz). This follows from the proportion of combined silica which is present, and which we may fairly assume to be a constituent of clay. In the table the amount of clay is calculated according to the composition of pure kaolin (kaolin equals SiO_2 46·4 per cent, Al_2O_3 39·7 per cent, H_2O 13·9 per cent). The balance which is left after deducting both free quartz and clay consists of free alumina and ferric oxide with water. This is really the substance of bauxite, with gradually decreasing proportion of alumina. The results of the analysis agree thus remarkably well with the theory according to which the low-level laterite is derived from the high-level laterite, and has during its transport to a new site taken up sand and clay as impurities. Further, the results show that the term laterite has a distinct meaning throughout the many varieties of this rock. Laterite is bauxite in various degrees of purity, from the richest wocheinite down to such specimens in which the free alumina has entirely disappeared. In this sense the specimen from Burmah which has been analysed by Captain James, and recorded in the Manual of the Geological Survey of India, is also still a true laterite. Its composition is similar to that of our two last specimens, No. 22 and No. 23. The sample contained 30·7 per cent quartz and 14·8 per cent clay, and the balance was made up almost completely of ferric oxide (47·4 per cent) with 4·7 per cent water and only 1·3 per cent free alumina.

It cannot be said with certainty what the state of hydration of the alumina is in these detrital laterites. They vary so much in composition, and the colours indicate that the ferric oxide may in some cases be anhydrous and in other cases be present as limonite. Taking all the specimens together, the average composition is such that there is about as much diaspore as there is gibbsite and about as much hematite as there is limonite.

As regards the method of analysis, we found fusion with hydrogen sodium-sulphate the best, if not the only method for all cases. By it the free silica is readily determined as distinct from the combined silica, the iron is obtained in solution, and so is the titanium. With larger proportions of titanium (1 per cent TiO_2 and upwards) we resorted to the method of separation by long-continued boiling, and small proportions of TiO_2 were determined colorimetrically by means of hydrogen peroxide.

To carry out this work at a distance from India would have been impossible, had we not received very liberal help in procuring specimens from a deposit which extends over an area of thousands of square miles. We desire to express our thanks to H.M. Secretary of State for India, through whose kind intervention the bulk of the very richest and most important specimens came into our hands; also to Mr. Edgar Thurston of Madras and to Dr. D. Hooper of Calcutta, who obtained for us the specimens by which the true nature of the high-level laterite was proved for the first time.—*Geological Magazine*, Decade IV., vol. x., p. 154.

ROBERT BOYLE AND THE WORD "BAROMETER."

By H. CARRINGTON BOLTON.

SINCE the publication of my note on the origin of the word barometer (CHEMICAL NEWS, vol. lxxxviii., p. 163) I have received a letter from Mr. A. Lawrence Rotch, of the Blue Hill Observatory, Massachusetts, communicating proof that the Hon. Robert Boyle had invented the term in 1665. The word is to be found in "The General History of the Air," which contains "A Short Account of the Statical Baroscope, Imparted by Mr. Boyle, March 24, 1665."

This "General History of the Air" is mentioned by Prof. G. Hellmann, the eminent bibliographer of meteorology, but he seems to have overlooked the letter quoted.

May 13th, 1903.

CARBONACEOUS SHALE FROM ARGENTINA.

By EDWY G. CLAYTON, F.C.S., F.I.C.

SOME specimens of carbonaceous shale from the Province of Rioja, Argentine Republic, have been examined by the writer. This shale is black, of resinous lustre, slightly greasy to the touch, and exceedingly friable. Heated in the absence of air it yields much gas, readily combustible with a highly luminous flame. The residuum of fixed carbon is not in the form of coke, but is mingled with the mineral matter as a dark grey powder.

Two samples of the shale on analysis gave the following results:—

	A.	B.	Mean of the two analyses.
Specific gravity	1·57	1·75	1 66
Moisture	1·69	1·74	1·72
Volatile combustible matter ..	20 10	17·08	18 59
Fixed carbon	33·86	30 30	32·08
Ash	44·35	50·88	47 61
	100·00	100·00	100 00
Volatile sulphur	1·14	0 63	0·89
Sulphur in ash	0·35	0·35	0·35
Total sulphur	1·49	0·98	1·24
Calorific power (determined approximately by L. Thompson's method)	3300	2750	3025

Certain of the figures are compared below with those in some published analyses (Groves and Thorp, "Chemical Technology," 1889, I., 48—49) of Scotch and Lancashire carbonaceous shales and cannel coal, the latter being included in the table for contrast:—

	Carbonaceous shales.						
		Scotch shales.		Lancs. shales.		Cannel coals.	
	Argentine shale.	Fife "Rums."	From the Stirlingshire coal field.	Birtledean.	Pendleton.	Scotch, Lesmahagow.	Lancashire, Arley.
Spec. grav..	1·66	1·69	2·34	2·39	2·64	1·228	1·27
Volatile matter ..	18·59	26·74	16 53	16·84	22·52	49·34	33·7
Fixed carbon	32·08	20·51	—	—	—	40·97	66·3
Ash	47·61	52·75	83·47	83·16	77·47	6·34	3 6
Sulphur ..	1·24	—	—	—	—	1·35	1·2

These figures well show how, in the shales, the proportions of ash exceed the percentages of fixed carbon and

volatile matter, respectively; the converse applying in the case of the cannel coals, in which the quantities of mineral matter are relatively small.

Chemical Laboratory,
32, Holborn Viaduct, London, E.C.,
May 9, 1903.

SEPARATION AND ESTIMATION OF ZINC BY THE ELECTROLYTIC METHOD.

By A. HOLLARD.

Nature of the Electrolyte.

1. Solution of the Double Cyanide of Potassium and Zinc with a Large Excess of Soda.

The principle of the estimation of zinc in solution of the double cyanide of potassium has been known for a long time. The present method has no other object than to regulate the conditions of working more precisely and to show how we have applied this method to the separation of aluminium from zinc, and of zinc from iron.

The solution of sulphate of zinc containing a slight excess of sulphuric acid, is treated with soda until alkaline. Then we add a quantity of soda at 15° B, varying from 15 to 80 c.c., then 10 c.c. of a solution of cyanide of potassium at 20 per cent. Dilute to 300 c.c. The zinc is deposited with a current of 0·1 ampère. The cathode, which is of platinum gauze, has been covered previously by electrolysis, with a layer of copper, to prevent the zinc from adhering to the platinum, as it would always leave traces behind.

The deposit is of a beautiful bluish white colour, and can be obtained very thick without any trouble. In this manner we can easily obtain deposits of 1 grm.

It is quite probable that heavier deposits could be obtained, but we have not tried.

This method is particularly useful for the separation of zinc from aluminium. The alloy of aluminium and zinc—we operate on 1 grm.—is attacked with aqua regia, treated with a mixture of sulphuric acid and water containing 2 c.c. of sulphuric acid at 66° B. After the attack the solution is evaporated until the appearance of voluminous white fumes; the residue, which contains only sulphates and a few drops of free sulphuric acid, is taken up with water; after solution, we add soda and cyanide, as has been described above. The electrolysis is then proceeded with in the manner described.

The separation of zinc and iron is easily effected by the cyanide method; the iron, which should be in the ferric state, is, in fact, insoluble in the presence of a large excess of soda.* As it retains zinc, even after electrolysis, we are obliged to filter off the precipitate of iron as soon as the electrolytic deposition of the zinc is effected, to re-dissolve it in the smallest possible quantity of sulphuric acid, neutralise with soda, and add to this liquid the mother-liquors which have already deposited their zinc on the cathode. The precipitate is left at the bottom of the glass, the electrodes are plunged in, and the electrolysis proceeded with, using the current already mentioned, viz., 0·1 ampère; the cathode is formed of the gauze which has been already used, and which is covered with the first layer of zinc. The remainder of the zinc is then deposited completely, at least when using the proportions of iron and zinc with which we have experimented (see experimental results). Good care must be taken in the separation of the zinc and the iron—as should always be the case when the electrolyte contains a precipitate—to allow the precipitate to settle at the bottom of the glass, and then to push the spiral down to the bottom of the precipitate; in this manner we remove, to a great extent, the metal that might be entangled.

The separation of zinc from nickel cannot be effected by this method; a small quantity of nickel is always deposited with the zinc.

Experimental Results.

The zinc used in these experiments contained 0·18 per cent of lead. The iron used was in the form of ferric sulphate.

	Amount taken. Zn.	Fe.	Deposit.	Fe.	Zn.
	Grm.	Grm.	Grm.	Grm.	Grm.
	With an Excess of 15 c.c. of Soda at 15° B.				
1.	0·3	0·1	0·3014 less	0·0016 gave	0·2998
2.	0·3	0·1	0·3022 ,,	0·0021 ,,	0·3001
3.	0·5	0·1	0·4982 ,,	0·0021 ,,	0·4961
	With an Excess of 80 c.c. of Soda at 15° B.				
4.	0·2993	—	0·3046 ,,	0·0004 ,,	0·3042
5.	0·3019	0·1	0·2962 ,,	0·0016 ,,	0·2946
6.	0·5007	0·01	0·5053 ,,	0·0004 ,,	0·5049
7.	1·0007	0·1	0·9939 ,,	0·0006 ,,	0·9933
	Zn.	Al.			
8.	0·1038	0·9	0·1079		
9.	0·1012	0·9	0·1051		
10.	0·5001	0·5	0·5094		
11.	0·4998	0·5	0·5058		
12.	—	2	0·0004		

(No. 12 was taken from the same ingot as the preceding portions of Al).

2. Solution of Sulphate of Zinc treated with Organic Salts, and a Slight Excess of Acetic Acid.

This method is not applicable in the presence of iron—which reduces its importance considerably. In fact, the iron has a tendency to decompose partially with the zinc, not to the state of metallic iron as we stated in error (*Bull. Soc. Chim.*, vol. xvii., p. 887), but to a state of oxidation or saline combination that we have not been able to determine.

In the absence of iron this method is good. The instructions given in our previous paper (*loc. cit*) must be followed, with the exception that the electrodes must be made according to our new system, with the cathode of platinum gauze, and the current should be 1 ampère. Care must be taken to cover the cathode with copper before depositing the zinc, to prevent the latter adhering to the platinum.

The separation of zinc and aluminium is difficult to effect by this method, on account of the precipitation of alumina during the electrolysis, which precipitation may carry down zinc. This difficulty is also met with when using the oxalate method.

Experimental Results.

The zinc used in these experiments contained 0·18 per cent of lead.

	Amount taken. Grm.	Deposit.
1. Zn	0·5000	0·5031
2. Zn	0·5000	0 5039
3. Zn	0·3000	0·3027

—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 7.

* Actually, the iron is very slightly soluble; if we refer to the experimental results, we see that with the zinc there are deposited quantities of iron varying from 0·0016 to 0·0021 grm. when there is 15 c.c. of soda in excess, and from 0 0004 to 0 0016 grm. with an excess of 80 c c. of soda. Thus a large excess of soda is rather favourable; this has also been shown by the analysis of the mother-liquors, from which the zinc was removed by electr lysis.

Change of Address.—Mr. J. L. C. Eckelt informs us that he has removed his offices from 83, Prinzen-Allee to 19, Chaussee-Strasse, Berlin.

PROCEEDINGS OF SOCIETIES.

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

Centenary of the Announcement of the Atomic Theory by John Dalton.

"*The Atomic Theory.*"* By F. W. Clarke.

One hundred years ago, John Dalton gave before the Manchester Literary and Philosophical Society the first hint of his atomic theory.

It was only a preliminary notice; a mere note appended to a Memoir on another subject, and it attracted little attention. In 1808, however, he published his "New System of Chemical Philosophy," and since then the history of chemistry has been the history of the atomic theory. To celebrate Dalton's achievement, and to trace its influence upon science, is the purpose of this lecture.

The earliest recorded attempts to form an atomic theory were made by the Greek philosophers. Leucippus came first, to be soon followed by Democritus and Epicurus. Then came the Roman, Lucretius, who gave the doctrine the most complete statement of all. These attempts were all qualitative, and had little effect upon the development of science. They were mere speculations, of no direct utility to mankind; and they they gave rise to interminable controversies of a metaphysical character.

Early in the seventeenth century, Gassendi revived the atomic philosophy of Epicurus, and he was soon followed by Boyle, by Newton, and by many others. These men were the real precursors of Dalton, to whom their teachings were well known. In chemistry, the first atomistic treatise seems to have been written by Swedenborg, in 1721; something was done by Bryan Higgins, of London, in 1775, and a better statement was published by William Huggins, of Dublin, in 1789. None of these attempts were effective, however, and none of them lead to discoveries. The time was not ripe, the data were too few; but the right moment came to Dalton, who knew how to use it well. Dalton established on a firm basis the law of definite proportions, and then the law of multiple proportions, and finally he discovered that to every chemical element a definite combining number, the relative weight of its atom, could be assigned. This new atomic theory, which figured chemical union as a jutaposition of atoms and gave to every atom a definite weight, put chemistry for the first time upon an absolutely general quantitative basis. Dalton thus created a working tool of extraordinary power and usefulness; something which none of his forerunners had been able to do. In the growth of chemistry, since his day, the guiding clue has been the atomic theory.

The development of the new doctrine followed two distinct lines; one chemical, the other physical. On the chemical side, Berzelius made many determinations of different atomic weights, invented symbols, and devised the system of chemical formulæ and equations which, somewhat modified, is now everywhere in use. On the physical side, Gay-Lussac connected the new atomic weights with the densities of the gases, and Avogadro, introducing into science the distinction between atoms and molecules, discovered a fundamental law. Equal volumes of gases, under equal conditions, contain equal numbers of molecules. In 1819, Dulong and Petit discovered the law connecting the atomic weights of the elements with their specific heats, and this law, with Avogadro's, ultimately gave the atomic theory its present form.

From 1820 until 1850, the growth of chemistry was mainly on the organic side; but every step forward was dependent upon Dalton's theory. The conceptions of compound radicals, the laws of substitution, and the theories of chemical structure were among the great advances mentioned. The discovery of isomerism, of the fact that two radically different compounds may contain the same elements in exactly the same proportions, was especially important. The same atoms were differently arranged, and on that supposition only could the phenomena be explained. Without the atomic theory organic chemistry would be quite unintelligible; a mere dust heap of unrelated facts.

Between 1850 and 1860, it was found, through the labours of several chemists, notably Frankland and Kekulé, that every elementary atom had a definite capacity expressible by number for combining with other atoms. From this conception important consequences followed; some of them industrial, and others more purely scientific. This subject was quite fully discussed by the lecturer, who then passed on to another question, that of relations between the atomic weights of the different elements. Through investigations of this class, Mendeleeff in 1869 discovered the periodic law, and showed that all the properties of the elements were dependent upon the atomic weights. Furthermore, Mendeleeff, finding gaps in his classification, predicted the existence of three unknown metals and foretold their properties. This extraordinary prophecy has since been completely fulfilled, and the three metals gallium, scandium, and germanium are now well known. In short, the properties of all substances are intimately connected with their atomic or molecular weights, so that the set of numbers discovered by Dalton are the fundamental constants of all exact chemistry.

The acceptance of Dalton's atomic theory leads at once to two other problems of great interest. What is the nature of the atom? And is all matter *one* at bottom, or of many kinds? On the latter subject most philosophical chemists are now of the belief that our elements are not ultimate; and the only evidence in favour of their elementary nature is the fact that with our present resonrces we are unable to decompose them. On the other hand, they are connected by so many close relations that something belonging to them in common must underlie them all. Several lines of evidence bearing upon this side of the question were cited, and among them the evidence of the spectroscope as applied to the heavenly bodies. The nebulæ are chemically simple; the hotter stars more complex; the finished planets most complex of all. It is possible, then, that the evolution of planets from nebulæ has been accompanied by an evolution of the elements themselves.

If these considerations are valid, then the Daltonian atoms must be complex bodies. J. J. Thomson, of Cambridge, has recently shown that bodies smaller than atoms can be identified by electrical means; Prof. Rutherford, studying the phenomena of radio-activity, has obtained evidence pointing in the same direction; and it begins to seem probable that radio-activity is a phenomenon of atomic decay. An actual breaking down of the heavier atoms seems to be almost within our reach. But all investigations of this sort are so new that we must hold our opinions concerning them open to revision.

As to the nature of the atom, the lecturer referred to Lord Kelvin's theory that they may be vortex rings in the ether; to Prof. Larmor's conclusion that they are centres of strain in the ether; and to Prof. Osborne Reynolds's recent remarkable theory which derives them from irregularities in a universal granular medium. His own opinion coincides with J. J. Thomson's conclusion, that the atoms are clusters of small corpuscles, for this best harmonises with chemical data. The ultimate corpuscles are all equal to one another; that is, they are all alike.

In conclusion, Prof. Clarke reiterated his statement as to the fundamental importance of the atomic weights, and urged the importance of their more exact measurement. To this end he advocated co-operative research between all workers in this field, and the endowment of laboratories. Who will establish the Dalton laboratory for pure research?

* The Wilde Lecture.

NOTICES OF BOOKS.

Quantitative Chemical Analysis by Electrolysis. By Alexander Classen. Authorised translation. Fourth English from the Fourth German Edition, Revised and Enlarged, by Bertram B. Boltwood. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. Pp. vii.—315. 8vo. Illustrated.

Prof. Classen's standard work here named is so well known, both in Germany and in English-speaking lands, that mere announcement of a fourth edition will interest the many already using it; this new edition contains many additional electro-analytical processes which have been invented since 1897. In preparing the English translation Dr. Boltwood had the privilege of using Prof. Classen's new work, "Select Methods in Analytical Chemistry," published in 1902, as well as of Hastings and Beach's "Text Book of General Physics."

Those familiar with the former editions will remember the clear descriptions of apparatus and methods in the first eighteen chapters and the numerous references to literature in the special part. The author shows his appreciation of bibliography so strongly that it seems unfortunate that the brief Historical introduction contains no reference to original papers, even when dates are given.

It must be gratifying to Americans to notice how frequently methods devised by Prof. Edgar F. Smith, of the University of Pennsylvania, are cited with approbation.

A few full-page illustrations, from photographs, assist in elucidating the subject.

Two indexes, one to Authors and one of subjects, both alphabetically arranged but separately printed close this valued work, but why separate into two divisions an alphabetical index? H.C.B.

The Principles of Physical Chemistry. ("Traité de Chemie Physique; Les Principes"). By Jean Perrin. Paris: Gautier-Villars. 1903. Pp. 299.

The principles, of which the discussion and examination form a natural introduction to the different physical sciences, are the subject of this volume. The philosophical value of these principles lies in the fact that every one of them is suggested by the simple comparison of known facts, without the necessity of representing the world otherwise than it appears to us. In opposition to this inductive method, there has developed another method which consists in imagining for matter, *à priori*, a structure of which the direct perception escapes our limited senses, and by which we are enabled to foresee the properties of matter by deductive means.

It cannot be denied that by the latter method much brilliant work has been accomplished and many facts foretold. In this volume the author deals entirely with the application of inductive methods, though he protests against a judgment which would condemn molecular theories *en bloc*, instead of being satisfied with pointing out the limits beyond which they cannot pass.

The book is divided into nine chapters, and these are each sub-divided into four or five sections. The first chapter is on the "Idea of Force," static, dynamic, &c. Chapter II., on "The Factors of Action," deals with tensions and pressure, electromotive force, temperature, radiation, and chemical action; then come two chapters on energy and work. Chapter V. is on the "Principle of Evolution," and Chapter VI. on the "Characteristics of Stable Equilibrium." The remaining chapters become a little more chemical in their characteristics, though everything is treated from a mathematical point of view; in fact, the whole volume is mathematical and theoretical in character, and can by no means be glanced through in a casual manner.

It is provided with a comprehensive table of contents, but, as is so often the case with foreign works, there is no index.

The General Laws of the Action of the Diastases. ("Loi Générales de l'Action des Diastases"). By Victor Henri. Paris: A. Hermann. 1903. Pp. 129.

Among the phenomena which take place in the living organism, the processes of nutrition, of absorption, of secretion, and of support of the cells of the organism, in fact, the whole of the metalbolism of the living body, may be considered as being almost entirely reducible to diastasic action. As experimental researches increase, the number of actions, considered previously as being intimately connected with the vitality of certain cells, diminish. The subject of the present volume is the examination of the laws governing diastasic action, and the plan adopted is to examine the action of diastases by means of the methods and results obtained by means of physical chemistry; these methods are referred to briefly in the introduction.

Only three diastases have been considered in this volume—invertine, emulsine, and amylase. These diastases have the advantage of enabling a quantitative examination of their action to be made with greater ease than with most other diastases. Still, only the first portion of the experimental examination of diastasic action is contained in the present volume; for instance, the effect of temperature and the different conditions of the medium used have not been dealt with. But in spite of this, the author has put forward a general theory of diastasic action, which brings these effects completely within the range of general chemical laws. He proposes to classify catalytic action under the five following headings:—1. Pure catalysis by simple presence. 2. Auto-catalysis. 3. Formation of intermediate compounds produced very rapidly; these compounds may be complete or incomplete. 4. Intermediate compounds produced slowly. 5. Action of a catalysing agent on a series of successive reactions.

Photographic References for 1903. ("Aide-mémoire de Photographie pour 1903"). Published under the Auspices of the Photographic Society of Toulouse. By C. Fabre. Twenty-eighth Year. Third Series, Vol. VIII. Paris: Gautier-Villars. 1903. Pp. 340.

This annual, which is the oldest French publication of its kind, has just been published. The beginner as well as the practised operator will find many practical hints which will be of use to them during the coming season. As in previous editions, the author does not limit himself to a bare statement of formulæ, &c., but he also gives useful advice as to manipulation so as to obtain good negatives and satisfactory pictures.

Die Grundzüge der Chemischen Didaktik. ("The Outlines of Chemical Didactics"). By Dr. A. Wolfrum. Leipzig: Wilhelm Engelmann. 1903.

This book has been written for the purpose of advising students of chemistry, or those who are about to take up the study, concerning their subject, and the best and most rational way to make the most of the time they have to devote to it. The whole spirit of the book tends to set a high ideal before the student, and to stimulate his mental activity. A complete plan of study is given, based upon practical experience, with hints on special requirements and details of examinations, as well as suggestions for the most profitable manner in which to set about original research, all of which throw incidentally an interesting side light on German aims and methods. The author also deals with laboratory instruction in its various aspects, the objects and usefulness of qualitative and

quantitative analysis and technical processes, with a short essay on the influence of the teacher on the special method of study adopted. No one will be found to deny that at any rate until very recently there has been urgent need of reform in methods of teaching chemistry, and this thoughtful study of a rational system will undoubtedly be found to contain many hints and valuable suggestions, by which both teachers and students may benefit.

Elektro-metallurgie. Die Gewinnung der Metalle unter Vermittlung des Elektrischen Stromes. Erste Abtheilung. ("Electro-metallurgy. The Preparation of Metals by means of the Electric Current." Part I.) By Dr. W. BORCHERS. Leipzig: S. Hirzel. 1902.

THIS is the third edition of Dr. Borchers' book, and has been considerably enlarged, and to a great extent re-written. Owing to the need for keeping pace with the rapid development of the subject, we should have thought that it would have been better to omit many of the descriptions of earlier processes in favour of an increased attention to more recent methods. This volume is the first part of the work, and includes the preparation by the help of the electric current of the metals of the alkalis and alkali earths, and also copper and nickel. Many of the processes described are rapidly becoming obsolete, being superseded by cheaper or more expeditious methods; but, on the other hand, in many respects the information is most concisely and well stated, as, for example, in the section on the preparation of cerium. The book is fully illustrated, and will be found specially suitable for use as a text-book of moderate difficulty.

Chemisches Praktikum. II. Teil. *Präparative und Fabrikatorische Ubungen.* ("Practical Chemistry. Part II. Preparations and Manufacturing Processes"). *Atlas zum II. Teil.* ("Atlas" to Part II.). By Dr. A. WOLFRUM. Leipzig: Wilhelm Engelmann. 1903.

THE second part of Dr. Wolfrum's work on practical chemistry deals with manufacturing processes and methods of preparation generally; the illustrations are collected in a separately bound Atlas, arranged specially for use with the text-book, a plan which seems to have a good deal to recommend it. The first section of the book describes the treatment of substances by mechanical means, preparatory to their subjection to chemical processes, with the various methods of attaining the necessary conditions of reaction by mixing, shaking, distilling, &c. All these methods are fully illustrated in the atlas. The second section comprises a collection of methods of preparation of many inorganic and organic compounds, the latter of which will be found specially useful by teachers; by judicious selection a very instructive course of practical work in organic chemistry could be adapted from it. This section appears to be thoroughly systematic and accurate, and the various examples are always well chosen, sufficient details being given to enable the student to perform most of the operations without further instruction or assistance. The rest of the book is written from a more purely technical point of view, and summarises the facts influencing the choice of apparatus and machinery, their output and cost of maintenance, with many valuable hints to the managers of factories and works. The methods of preparation of various chemical products are described, rather too shortly, however, for practical purposes, owing to the comparatively small space necessarily allotted to this branch of the subject.

The Atlas contains some 700 illustrations of pieces of apparatus and machinery, and eleven tables to show the arrangement of more complicated plant; this Atlas will be found useful both for technologists and for laboratory purposes. The illustrations have been carefully prepared, except in a few cases, as, for example, that of the Soxhlet's apparatus on page 41, which would probably not be clear to those who had not previously handled the apparatus in some form.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 17, April 27, 1903.

Catalytic Decomposition of Alcohols by Finely-divided Metals. Allylic and Benzylic Alcohols, Secondary and Tertiary Alcohols.—Paul Sabatier and J. B. Senderens.—In recent papers the authors showed that copper prepared by reduction of its oxide caused a regular decomposition of formenic primary alcohols into aldehyde and hydrogen at a temperature below 300°. At higher temperatures, or in the presence of reduced nickel or platinum sponge, instead of aldehyde, the products of its decomposition are carbonic oxide and hydrocarbons. The authors now extend their research, using allylic and benzylic alcohols. In the case of secondary alcohols, a regular decomposition takes place into acetones and hydrogen, the stability of the acetones being greater than that of the aldehydes. Tertiary alcohols, under similar conditions, are transformed into water and ethylenic carbides.

Cementation of Iron.—Georges Charpy.—The cementation of iron is not only caused by the solubility of carbon in iron; it can be produced either under peculiar conditions, especially at low temperatures, by the transformation of iron into iron carbide, which is a meta-stable body, or under normal conditions by the indefinite transformation of carbon into graphite through the medium of a limited quantity of iron.

Reduction of certain Metallic Halogen Compounds by means of Hydrogen. Influence of Pressure.—A. Jouniaux.—Glass tubes containing a metallic chloride, bromide, or iodide are filled with pure dry hydrogen under reduced pressure and then sealed. The absolute temperature of the gas is noted. The system is then raised to a high temperature, quickly cooled, and a volumetric analysis of the gaseous mixture obtained.

Electrolytic Reduction of Chlorate of Potash.—D. Tommasi.—During the electrolysis of a solution of potassium chlorate acidulated with sulphuric acid, an oxidation or reduction of the chlorate takes place, according to the nature of the anode. When platinum electrodes are used, perchlorate is formed at the anode without a trace of chloride at the cathode. With a cathode of platinum and an anode of zinc, potassium chloride is produced at the anode only, with no reduction of chlorate at the cathode. The reduction in this case is attributed, not to hydrogen, but to zinc; this latter substance combining with the oxygen of the chlorate to form zinc oxide, and so reducing the chlorate to chloride:—

$$KClO_3 + 3Zn = KCl + 3ZnO.$$

$$3ZnO + 3H_2SO_4 = 3ZnSO_4 + 3H_2O.$$

If a solution of chlorate containing no sulphuric acid is used, a white precipitate of zinc hydrate is seen at the anode. Potassium perchlorate, when electrolysed in the same manner as the chlorate, undergoes no reduction.

A Reaction by which Symmetric Diphenyl Pyrones are Produced.—R. Fosse.—The author devises a general method of preparation of the diphenyl pyrones. This consists in treating the orthophosphoric ethers of phenols at a high temperature with potassium carbonate. This carbonate reacts equally on the salicylic ethers, and the following rule can be formulated:—At a temperature below their boiling- or decomposition-point, the diphenyl carbonic ethers and the salicylic ethers (salols and salicylates of alcohols), when heated with the alkaline carbonates, undergo a transformation, with evolution of carbon dioxide gas.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 23.

Preparation and Properties of Hydride of Potassium.—Henri Moissan.

Preparation and Properties of Hydride of Sodium.—Henri Moissan.

New Synthesis of Formic Acid.—Henri Moissan.

Action of Hydride of Potassium on Iodide of Ethyl and Chloride of Methyl. New Preparations of Ethane and Methane.—Henri Moissan.—The above four papers have been already noticed in these columns.

Action of Hydrochloric Acid on the Sulphates of the Sesquioxides of Aluminium, Chromium, and Iron.—A. Recoura.—Already inserted in full.

Mutual Isomerations of the Acylacetylacetic Ethers.—L. Bouveault and A. Bongert.—The authors have endeavoured to find out whether they could apply MM. Claisen and Haase's method of partially transforming the *o*-acetylacetylacetate of ethyl into its isomer the diacetylacetate, to the substances which have formed the subject of their own researches. For this purpose they prepared the *o*-butyrylacetylacetate of methyl already described by them, and following the method given by the above-mentioned chemists, they obtain 70 per cent of the theoretical amount of pure *o*-butyrylacetylacetate of methyl, showing that the method can be generalised. To transform the *o*-butyrylacetylacetate of methyl into the *c*-acylised derivative, they again followed the general method described by the German chemists with satisfactory results.

Action of Fuming Nitric Acid on the Acylacetylacetates and the Acetylacetates of Methyl and of Ethyl.—MM. Bouveault and A. Bongert.—Brown fuming nitric acid was added, a little at a time, to C-butyrylacetylacetate of ethyl. The action proceeds as in ordinary nitration; the mixture is then poured into water, and this water shaken up with ether, and the ether is washed successively with water, carbonate of soda in excess, and again with water; the ether is then driven off on the water-bath. A mobile liquid remains, which, contrary to expectation, distils *in vacuo* without any decomposition. In this manner a rather thick liquid is obtained, boiling at 170—171° under 23 m.m. It is of a light amber colour, and possesses a peculiar though not very penetrating odour, and causes itching on contact with the skin. It corresponds to the formula $C_4H_5NO_3$. However, its molecular weight, determined by cryoscopy in benzene, shows that its formula ought to be doubled, $C_8H_{10}N_2O_6$. It is not easy to account for the formation of this body by means of an equation, but the authors repeated the experiment with C-butyrylacetylacetate of methyl, and obtained a liquid resembling the previous one but boiling at 151° under 10 m.m. Its composition corresponded to $C_3H_3NO_3$, which, according to cryoscopic observations, must also be doubled, $C_6H_6N_2O_6$. As the original bodies were an ethylic and a methylic ether, differing from each other only by CH_2, and as the two products differ by C_2H_4, it follows that these latter bodies both contain the ether group twice. Therefore the formula of the former must be written $C_2N_2O_2(CO_2C_2H_5)_2 = C_8H_{10}N_2O_6$, and that of the latter $C_2N_2O_2(CO_2CH_3)_2 = C_6H_6N_2O_6$. The mechanism of these two reactions becomes clear, and may be represented by the following equations :—

$$2CH_3-CO-\underset{\displaystyle CO-C_3H_7}{\overset{\displaystyle |}{CH}}-CO_2CH_3 + 2NO_3H =$$
$$= 2C_3H_7-CO_2H + 2CH_3-CO_2H + C_2N_2O_2(CO_2CH_3)_2,$$

and—

$$2CH_3-CO-\underset{\displaystyle CO-C_3H_7}{\overset{\displaystyle |}{CH}}-CO_2C_2H_5 + 2NO_3H =$$
$$= 2C_3H_7-CO_2H + 2CH_3-CO_2H + C_2N_2O_2(CO_2C_2H_5)_2.$$

Examination of the Product of the Nitration of Acetylacetic Ether.—J. Bouveault and A. Bongert.—Already noticed.

Preparation of Tetrachlorophenol.—Et. Barral and E. Grosfillex.—Contrary to the expectations of several chemists, the authors have succeeded in transforming synthetic phenol into tetrachlorophenol by means of a current of chlorine without addition. They effected this in four different manners :—(1) In the presence of chloride of antimony; (2) in the presence of iodine; (3) in the presence of anhydrous perchloride of iron; and (4) by direct chlorination. The purification of tetrachlorophenol is a long and difficult operation; mediocre results were obtained by distilling the product with water, and bad results by distilling *in vacuo*. The use of different solvents, such as benzene, alcohol, or chloroform, did not give any results, both the product itself and the impurities accompanying it being too soluble. The best method is to treat it with petroleum ether, which removes 10 or 15 per cent of the tetrachlorophenol as well as black and red oily impurities, and then dissolve the remainder in a 5 per cent solution of caustic soda; binoxide of sodium is then added, about 10 per cent of the weight of the tetrachlorophenol, and after twelve hours the liquid becomes bright yellow in colour. It is filtered and hydrochloric acid added, drop by drop; filter again, then add an excess of hydrochloric acid to precipitate the whole of the tetrachlorophenol; the latter is dried *in vacuo* over H_2SO_4, and crystallised in petroleum ether, which gives long, white needles, fusible at 67—68°. The return of tetrachlorophenol varies from 75 to 85 per cent.

Acetamido-*p*-benzoyl-β-naphthol and Benzoylamido-*p*-benzoyl β-naphthol.—F. Reverdin and P. Crépieux.—The chloride of *p*-nitrobenzoyl was condensed with β-naphthol for about a quarter of an hour while heating. The product of the reaction was cooled, filtered, and washed with soda-lye, diluted until it did not dissolve the β-naphthol; it was then purified by crystallisation in acetic acid. The *p*-nitrobenzoyl-β-naphthol thus obtained is in the form of yellow needles, slightly soluble in alcohol, fairly soluble in acetone and benzene; it crystallises well in ligroïn, and fuses at 160°. The acetamido-*p*-benzoyl-β-naphthol is obtained by heating the base to boiling with acetic anhydride in the presence of acetate of soda; to prepare the benzoyl amido-*p*-benzoyl-β naphthol the base is dissolved in the necessary quantity of alcohol, then heated to boiling, and an excess of chloride of benzoyl added. The benzoylised derivative is deposited in the hot liquid, and the product of the reaction takes the form of a white crystalline mass; it is boiled again for a few moments, and filtered by means of the pump. It crystallises in benzene, in which it is slightly soluble, in white needles, fusible at 210°.

MISCELLANEOUS.

The Acid Nature of Acetylene.—Jean Billitzer.—The author has examined the solubility of acetylene in water and in variously concentrated solutions of KOH, NaOH, $Ba(OH)_2$, $Ca(OH)_2$, NH_4OH, H_2SO_4, $CH_3.CO_2H$, and Na_2SO_4. With the exception of baryta and ammonia, all these bodies diminish the solubility of acetylene. We see by this that the influence exercised on the solubility of a substance by the addition of electrolytes is not a simple phenomenon; if we wish to show the specific action of the substance in question it is necessary to compare it, from this point of view, with another body which behaves in the same manner with various electrolytes. If we examine acetylene and ethylene simultaneously, as they fulfil this condition, the comparison of their curves of solubility shows that acetylene is an acid, though a weak one, capable of giving rise to the anions $C\equiv CH'$ and $C\equiv C''$.—*Zeit. Physik. Ch.*, vol. xl., p. 535.

Contribution to Our Knowledge of Cæsium Compounds.—C. Chabrié.—The cæsium used in these experiments was extracted from American pollux, which contains about 13 per cent of Cs_2O; the mineral is attacked with hydrofluoric acid in a tall, narrow platinum crucible; the solution is freed from the heavy metals, then treated with carbonate of ammonium, and evaporated to dryness; the residue is taken up with water, and the filtered solution is evaporated again to dryness; the new residue is finally treated with boiling alcohol, which dissolves the carbonate of cæsium. The author has prepared the following salts:—Bromide of cæsium, CsBr, by the double decomposition of $BaBr_2$ and SO_4Cs_2, in isotropic crystals. The iodide, CsI, in cubical crystals. The fluoride, CsFl, by the decomposition of the fluorhydrate in an atmosphere of hydrofluoric acid in cubical crystals; the hydrofluorate, CsFl,HFl, obtained from CO_3Cs_2 and HFl, forms exceedingly hygroscopic crystals. The neutral chromate, CrO_4Cs_2, from CrO_4Ag_2 and CsCl, gives long yellow needles. The bichromate, $Cr_2O_7Cs_2$, gives orange-red crystals. The bisulphite, SO_3CsH, is formed by the saturation of CO_3Cs_2 dissolved in alcohol at 99°, by means of SO_2; it forms white crystals, very soluble in water, slightly soluble in alcohol. The sulphite, SO_3Cs_2, formed from the preceding salt and CO_3Cs_2 in alcoholic solution; if the preparation of the sulphite and the bisulphite of cæsium is effected in water, these salts are obtained mixed with a certain quantity of sulphate. Hyposulphite, $S_2O_3Cs_2$, in small needles very soluble in water. Hyposulphate, $S_2O_6Cs_2$, in hexagonal plates belonging to the rhombohedric system. Metavanadate, VaO_3Cs, from Va_2O_3 and CO_3Cs_2.—*Ann. Chim. Phys.*, Series 7, vol. xxvi., June, 1902.

The Decomposition of Mixed Hydrated Crystals.—R. Hollmann.—When two salts ($MnSO_4$ and $CuSO_4$, for example) possess two kinds of isomorphous hydrates, and, consequently, are able to form two kinds of mixed hydrated crystals ($[MnCu]SO_4\,7H_2O$ and $[MnCu]SO_4,5H_2O$), the curves representing the states of equilibrium between these crystals and their solution may correspond to three distinct types, analogous to those which Bakhuis Roozeboom met with in the case of the anhydrous mixed crystals; it may happen that the points of decomposition (temperature at which the higher hydrates decomposes into the lower hydrate and solution) of the mixed crystals may be situated between those of the two component salts, or even that the curve of decomposition (constituted from the points of decomposition relative to the different compositions of the mixture) may show a maximum; or again, that the same curve may show a minimum. The case of the sulphates of Mn and Cu belongs to the second type, that of the sulphates of Mn and Zn belongs to the first. As for the composition of the mixed crystals of the two hydrates, we may state the rule that the mixed crystals of the higher hydrate differ from those of the lower hydrate by a greater richness in that component of which the addition raises the point of decomposition. The gaps often observed in the series of mixed crystals depend essentially on the temperature, so that, by a suitable choice of the isotherm to be described, we are able to obtain complete series of mixed crystals of one or the other hydrate.—*Zeit. Physik. Ch.*, vol. xl., p. 561.

MEETINGS FOR THE WEEK.

TUESDAY, June 2nd.—Royal Institution, 5. "The Work of Ice as a Geological Agent," by Prof. Edmund J. Garwood, M.A.

THURSDAY, 4th.—Royal Institution, 5. "Electric Resonance and Wireless Telegraphy," by Prof. J. A. Fleming, F.R.S., &c.

—— Chemical, 8. "Imino-ethers corresponding to Ortho-substituted Benzenoid Amines," by G. D. Lander and F. T. Jewson. "Formation of an Anhydride of Camphoryloxime," "The Mutarotation of Glucose as Influenced by Acids, Bases, and Salts," and "The Solubility of Dynamic Isomerides," by T. M. Lowry. "Isomeric Partially Racemic Salts containing Quinquevalent Nitrogen—Part X., The Four Isomeric Hydrindamine *d*-Chlorocamphorsulphonates, $NR_1R_2H_3$," and "Isomeric Compounds of the Type $NR_1R_2H_3$," by F. S. Kipping. "The Hydrolysis of Ethyl Mandelate by the Fat-splitting Enzyme Lipase," by H. D. Dakin.

FRIDAY, 5th.—Royal Institution, 9. "The New Star in Gemini," by Prof. H. H. Turner, D.Sc., F.R.S.

SATURDAY, 6th.—Royal Institution, 3. "The 'De Magnete' and its Author," by Prof. S. P. Thompson, F.R.S.

Re Pirie *v.* The Company and Others.—The Electro-Chemical Co. (1900), Ltd., 1901, E. 85.—By orders of Mr. Justice Farwell.

Mr. F. J. TERRY HORSEY, of the firm of Messrs.

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THE CHEMICAL NEWS

VOL. LXXXVII., No. 2271.

THE USE OF THE ZINC REDUCTOR IN THE ESTIMATION OF VANADIC ACID.*

By F. A. GOOCH and R. D. GILBERT.

THE reduction of vanadic acid to the condition of vanadium tetroxide preparatory to estimating it by titration with potassium permanganate is generally accomplished by the use of sulphurous acid or hydrogen sulphide. The more convenient method of treatment by zinc and free acid is not directly applicable on account of the irregular reduction of vanadic acid under the conditions to a stage approximating that of the dioxide, as was first shown by Czudnowicz (*Ann. Phys.*, 1863, cxx., 39). The work herein described is the result of an attempt to find a reliable method for bringing the product of reduction of vanadic acid by zinc and acid definitely to the condition of the tetroxide, in order that the reductor so useful in the preparation of salts of iron for titration by potassium permanganate may be made similarly applicable in the estimation of vanadic acid and its salts.

A very convenient form of reductor (described in Blair's "Chemical Analysis of Iron," edition of 1902, p. 93) was made as follows—The contracted end of a piece of glass tubing, 2 c.m. in inside diameter and 50 c.m. long, was sealed to stop-cock prolonged in a smaller tube, 0·5 c.m. in inside diameter, to a length of 24 c.m. At the point of contraction in the larger tube was placed a piece of platinum gauze, next to this a mat of fine glass-wool 2 c.m. in thickness, and upon the last a column 40 c.m. long of amalgamated zinc of a size to pass a sieve of eight meshes to the centimetre. The smaller tube passed through a rubber stopper fitted to a vacuum flask, and the last was connected through a pressure regulator with the vacuum pump. In using this apparatus the pump was started, the regulator set to give a pressure in the flask less than the outside pressure by an amount equal to 20 c.m. of water; the reducing column of zinc was warmed by passing through it hot distilled water followed by 100 c.m.³ of hot 1 per cent sulphuric acid, and then the solution of the salt of vanadic acid to be reduced was gradually drawn through the zinc in small portions, alternating with portions of the 1 per cent sulphuric acid amounting to 100 c.m.³. Finally, the column was washed down with 100 c.m.³ more of the dilute sulphuric acid and about 250 c.m.³ of hot distilled water. Throughout the entire series of operations care was taken to keep the zinc covered with liquid and so out of contact with the air.

The lavender solution collected in the flask contains vanadium dioxide, which when exposed to the action of a current of air takes, as Roscoe has shown (*Ann. Pharm*, Suppl, 1868, vi., 98), the blue colour of the tetroxide. The first attempts, therefore, to bring about definiteness of condition were made along the lines of Roscoe's observation. The solutions obtained in the receiving flask were treated by air at various temperatures and for various lengths of time, and then, after heating to 80°, were titrated with nearly N/20 potassium permanganate standardised by reference to N/20 arsenious oxide.

This most exact method of standardising the permanganate was carried out by adding a convenient volume (43 c.m.³) of the permanganate to a solution of potassium iodide (3 grms.) acidulated with sulphuric acid (3 c.m.³ of the 1 : 1 acid) contained in a glass-stoppered flask fitted with a funnel tube and trapped, introducing through the funnel tube an excess of a standard solution of N/20 arsenious oxide, neutralising with acid potassium carbonate, and titrating in presence of starch with iodine also standardised against the arsenious oxide.

In blank experiments made from time to time with the reductor it was found that the reading colour developed in the acid solution only after the addition of 0·2 c.m.³ of the standard permanganate, and this correction, due to traces of iron in the zinc and the considerable volume of the solution, was applied in the experiments in which the vanadium salt was treated. In our experiments ammonium vanadate was the salt of vanadic acid employed, and the sample with which we worked contained 76·66 per cent of V_2O_5, as determined according to the iodometric method of Holverscheit (Inaug. Diss. Berlin, 1890, p. 49.

The results of some attempts under most favorable conditions to effect the oxidation of the reduced trioxide to the condition of the tetroxide by the action on air are given in Table I. These show plainly that, although the oxidation by air appears to proceed rapidly at the outset, the complete conversion of the lower oxides to the tetroxide by such action takes place with too great slowness and uncertainty to form the basis of a reliable and rapid quantitative method.

TABLE I.

Time of treatment by air. Minutes.	Temperature.	V_2O_5 taken. Grm.	V_2O_5 found by titration with $KMnO_4$. Grm.	Error. Grm.
75	56—28°	0·0767	0·0778	+0·0011
75	60—29	0·0767	0·0805	+0·0038
75	48—29	0·0767	0·0829	+0·0062
75	*100°	0·0767	0·0772	+0·0005
75	*100	0·0767	0·0769	+0·0002

* Brought twice to the boiling-point during this interval.

The action of the molecular oxygen of the air is obviously insufficient to bring about the complete oxidation of the lower vanadium oxides in acid solution to the condition of the tetroxide within a reasonable time, and ordinary oxidisers carry the action too far, oxidising the tetroxide as well as the lower oxides. We have found, however, that silver oxide and silver salts will supply oxygen in a condition of activity sufficient to affect the lower oxides easily while leaving the tetroxide intact. Silver sulphate appears to be the most convenient form in which to use the silver compound.

In making our experiments with silver sulphate the solution of the vanadic acid was treated in the reductor in the manner described, except that the receiving flask was charged at the outset with a saturated solution of silver sulphate—100 c.m.³ in each of the first six experiments, 300 c.m.³ in the last two. The contents of the flask were boiled and then filtered upon asbestos in a perforated crucible. The solution, now about 700 c.m.³ in volume, was heated again to the boiling-point and titrated with N/20 potassium permanganate. When the reduced solution issuing from the reductor meets the silver sulphate a muddy deposition of finely-divided silver begins; but upon boiling the mixture the metallic silver gathers into a single spongy mass and leaves the solution so clear that were it not that spongy silver is easily acted upon by the permanganate the titration might be made without previous filtration (Giles, CHEMICAL NEWS, 1867, xv., 204; Otto van der Pfordten, *Ber.*, xx., 3375; Friedheim, *Ber.*, xx., 2554).

TABLE II.

V_2O_5 taken. Grm.	$KMnO_4$ required, nearly N/20. C.m.³.	V_2O_5 found. Grm.	Error. Grm.
0·0767	17·	0·0770	+0·0003
0·0767	17·04	0·0771	+0·0004
0·0767	17·05	0·0772	+0·0005
0·0767	16·96	0·0768	+0·0001
0·0767	16·98	0·0769	+0·0002
0·0767	17·	0·0770	+0·0003
0·1918	42·9	0·1942	+0·0024
0·1918	42·7	0·1933	+0·0015

* Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, xv., p. 389.

The results of these experiments are given in the accompanying table. For the smaller amounts of vanadium the determinations are accordant and exact. The wider variations in the last two experiments are probably due to the difficulty of catching the pink end-reaction in presence of the reddish yellow colour which appears as the vanadic acid is formed in considerable amount. This is a difficulty inherent in the permanganate process of titration when large amounts of vanadic acid are involved.

METHODS FOR THE ESTIMATION OF GUTTA-PERCHA.

By Dr. ED. MARKWALD and FRITZ FRANK.

The information met with in chemical literature on the properties and estimation of gutta-percha is fairly considerable, but it is rather indefinite and but slightly concordant.

Thus, according to Payen (*Comptes Rendus*, vol. xxxv., p. 109), ether dissolves only a part of the gutta, while Arppl (*Dingl. Polytech. J.*, vol. cxxi., p 442) observed complete solution when the ether is anhydrous and free from alcohol; alcoholic ether leaves portions undissolved. More recently Obach ("La Gutta-percha," 1899, p. 25) gives gutta-percha, or at least the hydrocarbon portion of the natural product, which is the true gutta-percha, as entirely soluble in ether which would only dissolve the resins albane and fluavile.

The technical works are full of contradictions of this kind.

As methods of estimation, properly so called, we would mention that of Henriquès, who dissolves the resins by extraction with ether, petroleum ether, or acetone, and weighs them directly by evaporating the solvent, or indirectly by the loss of weight of the gutta extracted. Then he takes up the latter with sulphide of carbon or chloroform, filters, distils, and dries *in vacuo*.

Obach's method hardly differs from the preceding one: The material, dried and suitably pulverised, is extracted with ether or ligroïn. The resins are determined by the loss of weight of the substance dried until the weight is constant, or by direct weighing after the evaporation of the solvent. The gutta in the residue is dissolved with sulphide of carbon or chloroform, the organic detritus and other impurities are separated by filtration; the solution is then concentrated and the gutta precipitated with alcohol.

H. Borntraeger (*Gummi Zeitung*, 1899, p. 631) proposed another method, in all respects similar to the preceding ones.

Having had occasion, during the past few months, to make a large number of analyses of gutta-percha for which a close concordance of results was necessary, and having observed that we obtained, on the contrary, considerable differences between one estimation and another when using the known methods, we sought about for a more exact means of effecting the determinations. It is the result of this research that we are about to describe.

We observed that the methods of Henriquès and Obach erred especially in the extraction of the resins. If we employ maceration in the cold the resins are always incompletely dissolved. If we employ heat, with acetone, in a Soxhlet apparatus, the filaments of gutta, no matter how finely they are divided, soon agglomerate into a mass that the solvent is unable to penetrate; with petroleum ether, or ether, the extraction is not limited to the resins, but a variable portion of the gutta also is attacked by the solvent.

The second operation, solution of the residue from the previous extraction by sulphide of carbon or chloroform, filtration and precipitation by alcohol, is not easy to perform. If we use sulphide of carbon, the extreme volatility of the solvent complicates the operation. With chloroform a considerable weight of the solvent is required to obtain a solution sufficiently fluid to filter easily.

After having determined the proportion of water in the sample, by the known method, we proceeded as follows :—

A. *Solution in Chloroform. Precipitation with Acetone.*

About 2 grms. of dried gutta are dissolved in 15 cubic centimetres of chloroform, and the clarified solution is poured, very gradually and with constant stirring, into 75 cubic centimetres of acetone in a tared Erlenmeyer flask. The gutta separates in the form of a voluminous porous precipitate, which can be collected and washed with ease. The resins and fats remain dissolved, the mechanical impurities remain in suspension. After decantation into another tared flask, the gutta is washed with acetone and the liquors all added together.

The gutta is dried at 100° and weighed; the resins are treated in the same manner. If we wish to weigh the insoluble impurities, in the estimation of a raw gutta for example, the filtration must be done through a tared filter paper.

It will be observed that the acetone must not be poured into the chloroform solution, as in such a case the gutta would separate in a compact mass, retaining the resins which could not be entirely removed by the subsequent washings. The resulting errors amount to 5 per cent.

Narrow-necked flasks can be used advantageously for precipitating the gutta; they allow the cake of gutta to be separated more easily and more exactly from the washings by decantation. However, if a morsel of gutta escapes it is taken up, on the filter, by means of warm toluene, after the washing is completed; the toluenic solution is more easy to filter than the chloroformic one. This solution is added to the principal mass of gutta, before evaporation. By this method we can do several complete estimations in one day.

B. *Solution in Chloroform. Precipitation with Alcohol.*

Proceed as in A. The resinous fraction will always be found several per cents too low. We have observed that this is due to the fact that a part of the resins of the gutta is not soluble in cold alcohol, as has already been stated by Payen. By heating, better results are obtained; but the operation is longer and not so convenient

C. *Solution in Chloroform. Precipitation by Ether.*

Two grms. of dried gutta are dissolved in about 10 c.c. of chloroform. This quantity suffices in the present case, as we add the ether to the chloroformic solution, and not inversely as in case A. The first portions of the ether make the solution more liquid, before precipitation takes place. Then we add gradually 100 c.c. of ether. At first the liquor remains limpid; then, after about an hour, the gutta commences to separate out in a voluminous white mass, which completely fills the flask. The precipitation is complete in about twenty-four hours. Filter into a tared matrass, and wash on the filter; the contents of the filter are stirred with a thick stirrer each time until no more liquor runs through, before adding a fresh portion of the washing ether.

The united liquors are evaporated, and the residue of resins is dried at 100° and weighed.

The mass of gutta, contracting by desiccation, takes a normal appearance and can be separated quantitatively from the filter, or weighed in the latter, if it has been tared previously.

If we are operating on a raw gutta in which we have to estimate the insoluble impurities, we take up the cake of gutta with warm toluene and pass through the tared filter, &c.

The quantity of ether indicated for the precipitation cannot be diminished without inconvenience; the separation of the gutta would be incomplete and would take place very slowly. Thus, with 75 c.c. of ether, instead of

100 c.c., we obtained 3 per cent less. With only 50 c.c. the precipitation only commences after about forty-eight hours, and it is not complete even after six days.

D. *Solution in Petroleum Ether.*

In a small matrass, with a vertical condenser, we heat 1 grm. of the dried substance with 100 c.c. of petroleum ether boiling at 35—50° C. for one hour. At the end of this time the solution is complete, but after cooling the gutta separates gradually in the form of a voluminous white mass, filling the whole liquor.

After twenty-four hours the precipitation may be looked upon as complete; filter and proceed as in C.

The following are a few of many analyses we have done:—

1. *Purified Gutta of good quality.*

Process	A.	B.	C.	D.
Gutta	80·21	85·90	79·23	78·55
Resins (by difference)..	19·79	14·10	20 77	21 45
	100·00	100·00	100 00	100·00

2. *Raw Gutta charged with Resins.*

Process	A.	B.	C.	D.
Gutta	46·41	48·61	45·82	46·10
Resins (by difference)..	53·59	51·39	54·18	53 90
	100·00	100 00	100·00	100 00

We see that the methods A, C, and D give fairly concordant results. For reasons of convenience and for economy of solvent we prefer process A, which we recommend to the attention of chemists. We advise drying the precipitates of gutta as much as possible, *in vacuo*, at a temperature not exceeding 50—60°; but if an apparatus of the kind is not available, heating in the oven to 100° will suffice.—*Zeitschrift f. Ang. Chemie*, 1902, p. 1029.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, May 20th, 1903.

Prof. W. A. Tilden, D.Sc., F.R.S., President, in the Chair.

Mr. Francis Watts was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Colin Noel Bennett, 95, High Street, Camden Town, N.W.; William Hunter Gandey, Bradley Court, Mitcheldean, Gloucester; John Howard Linday, Fenton Hall, Great Fenton, Stoke-on-Trent; Arthur Moore, 83, Elgin Road, Seven Kings, Essex; Thomas Rhind, M.R.C.S., 69, Gloucester Road, Regent's Park; Charles J. Smith, Sunnydale, Walton New Road, Stockton Heath; Sidney H. Woolhouse, M.A., 2, Durham Road, Lower Edmonton, N.

The Dalton Centenary.

The President stated that, in company with Sir Henry Roscoe and Dr. T. E. Thorpe, Past-Presidents, Professor Frankland, Vice-President, Dr. Scott, Senior Secretary, and Sir William Ramsay, Foreign Secretary, delegates appointed by the Council, he had taken part in the celebration by the Literary and Philosophical Society of Manchester of the centenary of the enunciation of the Atomic Theory by John Dalton, and in the name of the Chemical Society had presented the following Address:—

The Chemical Society
to the
Literary and Philosophical Society of Manchester.
Greeting.

Recognising the Atomic Theory as having been the foundation of scientific chemistry, the Chemical Society desires to be associated with the Literary and Philosophical Society of Manchester in celebrating the centenary of its enunciation by

John Dalton.

The century which has elapsed since the recognition of the great generalisations which led to the establishment of the theory has afforded continuous proof of its importance throughout the whole domain of physical science, and especially of chemistry, every new development of which has served to consolidate its position.

The Chemical Society offers at the same time to the Literary and Philosophical Society, so much older than itself, an expression of hearty congratulations on having been the medium of the first publication of that theory to the world, and having for upwards of a century so honourably assisted in promoting scientific, literary, and philosophical inquiry, more especially in those early days before the time of Dalton, when the physical sciences were still unorganised and waiting for the firm and philosophical basis on which they now rest.

Signed on behalf of the Chemical Society,

William A. Tilden, President.
Horace T. Brown, Treasurer.
Alexander Scott, W. Palmer Wynne, } Secretaries.
William Ramsay, Foreign Secretary.

May 7, 1903.

He reminded the Society that John Dalton was born in 1766, and was therefore a young man when, in 1803, he communicated to the Literary and Philosophical Society a paper "On the Absorption of Gases by Water and other Liquids," to which is appended the first table of atomic weights. Dalton states in the preface to his "Chemical Philosophy," that a brief outline of his views and of the results of his experiments "was first publicly given in the ensuing winter in a course of lectures on natural philosophy at the Royal Institution in London." The first volume of the "Natural Philosophy," containing the well-known symbols of the atoms devised by Dalton, is dated 1808.

The President further announced that a bust of Dalton had been modelled with the aid of the Chantrey marble, and various authentic portraits, one of which a daguerreotype, is in the possession of the Society, and that the bust when finished would be offered to the Society, probably before the end of the session, by our Past-President, Dr. Thorpe.

Centenary of the Birth of Liebig.

The President then stated that he had a further agreeable announcement to make.

The bust of Liebig which was placed on the table is a gift which the Society owes to the generosity of our Fellow, Dr. Messel.

It was probably not generally known that this year, and nearly at this time, is the hundredth anniversary of the birth of the famous German chemist. The day of the month is usually stated to be May 12th, and this is the date given in Hofmann's lecture, delivered berore the Society in 1875, and is therefore probably correct. No time has therefore been lost in honouring this important event.

We in England should be among the first to acknowledge the debt which science and the world at large owes to Liebig. Sixty years ago, when at the height of his fame, he visited England, and although it is true that he found but little science in this country, he had many admirers here who assisted in promoting a knowledge of the principles of plant and animal physiology which had been so largely the product of his own researches. With the advance of time has come so much new knowledge that Liebig's teaching in connection with agriculture, physiology, and medicine seems now to be less influential than it was fifty years ago. We cannot, however, forget that his views represented at that time an immense stride in advance of the state of ignorance which previously

prevailed. As chemists, we more especially recognise our indebtedness to Liebig not only as one of the chief founders of modern organic chemistry, but as having given us the system of practical instruction which, in principle, has been adopted in all universities and chemical schools since his time. Whether any of the students who worked under his direction in the laboratory at Giessen still survive is uncertain, but those who went forth as teachers certainly transmitted to succeeding generations something of the spirit which animated all those who came under Liebig's influence.

Of the following papers, those marked * were read:—

*73. "*The Conditions of Decomposition of Ammonium Nitrite.*" By V. H. Veley.

The decomposition of ammonium nitrate into nitrogen and water proceeds according to the general law, $\log A/A-x=a\theta$, whether the reaction follows its normal course or is accelerated by the addition of another substance. The decompositon is either impeded or stopped by ammonia liberated in the solution by the addition of a metallic oxide, this effect being likewise produced by aliphatic, benzenoid, and pyridine amines, also by aromatic hydrazines, and to a less degree by oximes; it is temporarily accelerated by amides of the aliphatic series, but other amides are ineffective. Benzoic sulphinide ("saccharin"), the only imide tried, produces a considerable acceleration, but the reaction proceeds according to the general law.

It does not appear that solutions of ammonium nitrite, prepared from silver nitrite and ammonium chloride, become alkaline in the course of the decomposition. Incidentally it was shown that finely-divided barium sulphate, although producing no permanent effect when added to a solution of ammonium nitrite evolving nitrogen, nevertheless temporarily increased the rate of evolution of nitrogen, owing to some alteration in the amount of dissolved gas.

Discussion.

Dr. Divers thought from the results of the investigation by Dr. Haga and himself of the interaction of sulphurous and nitrous acids in presence of bases, that it was free nitrous acid which, by its action on ammonium nitrite or ammonia, gave rise to the production of nitrogen.

Dr. Lapworth said that Dr. Veley's observations recalled the work of Hantzsch and Schümann, who had shown (*Ber.*, 1899, xxxii., 1691) that the velocity with which diazotisation of aromatic amines takes place is accelerated by an excess of acid. This change is not, as usually represented, a decomposition of the nitrite of the base, but is the effect of free nitrous acid on the substituted ammonium salt, or, in other words, the result of the interaction of the substituted ammonium ions with unionised nitrous acid.

Dr. Veley agreed with Dr. Divers that the initial change in the decomposition of ammonium nitrite was the resolution of the salt into its constituent base and acid, as is also the case with ammonium nitrate. The nitrogen or nitrous oxide resulted from a subsequent interaction of the liberated ammonia with the nitrous or nitric acid respectively.

*74. "*Freezing-point Curves for some Binary Mixtures of Organic Substances, chiefly Phenols and Amines.*" By J. C. Philip.

When the initial freezing-points of a series of mixtures of two substances are determined, and these temperatures are plotted against concentration, a freezing-point curve is obtained which, in the simplest case, consists of two branches, starting from the freezing-points of the constituents and cutting each other at a eutectic point. If however, the two substances can unite to form a compound, the two branches are cut by another intermediate curve, which may sometimes have a summit.

Examples of the latter type of curve with an intermediate branch have been found by the author for the system phenol—urea, where the summit occurs with a mixture containing 33 molecular per cent of urea, and for the systems *p*-cresol—aniline, phenol—α-naphthylamine, phenol—*p*-toluidine, α-naphthol—*p*-toluidine, phenol—picric acid, in all of which cases the summit occurs when the compounds are in molecular proportion.

According to Roozeboom's theory, the summit of the intermediate branch is reached with a mixture corresponding in composition with the formula of the compound, and crystals of this compound separate from all mixtures falling within the limits of the intermediate branch. This view has been confirmed in the above cases by analysis of the crystals which separated when solidification began.

In the freezing-point curve for phenol—urea, the intermediate branch is cut abruptly at the summit by another branch ending, apparently, at the freezing-point of urea. Perhaps the most interesting freezing-point curve obtained was that for phenol—*p*-toluidine, inasmuch as the compound formed by these two substances exists in two modifications with an intermediate branch on the freezing-point curve corresponding with each variety. The compound of phenol and α-naphthylamine crystallises so slowly that it was found possible to realise considerable portions of the ordinary branches of the freezing-point curve underneath the intermediate branch and below the eutectic temperatures.

The compounds of *p*-cresol and aniline (plates; f. p. 21°), phenol and *p*-toluidine (plates; f. p. 29°), α-naphthol and *p*-toluidine (needles; f. p. 53·5°), phenol and picric acid (bright yellow needles; f. p. 83°) have not been previously described.

Discussion.

Dr. Lowry referred to the melting-point curves for mixtures of water with succinic and phthalic anhydrides recently plotted by van der Stadt (*Zeit. physikal. Chem.*, 1902, xli., 353). In these cases, the "compound" (that is, the acid) is much more stable and less fusible than its components, so that these only separate from the fused product when this consists of almost pure water or pure anhydride; the central portion of the curve thus extends from about 0 up to 96 or 98 molecular per cent of anhydride. Moreover, the extent to which the "compound" dissociates on fusion can be gauged from the form of the central portion of the curve; if there were no dissociation, this would consist of two intersecting lines, but if there is much dissociation the pointed crest becomes replaced by a rounded summit, and in extreme cases may even be reduced to a broad flattened convexity.

Mr. Crompton inquired whether the author had ascertained to what extent his results were in agreement with the Schroeder-Le Chatelier formula.

Dr. Desch referred to the interest which the author's results presented in connection with the study of metallic alloys, and inquired whether, in the cases examined, the descending and ascending branches of the freezing-point curve were represented by straight lines. In the majority of alloys, these branches are more or less curved, indicating the formation of solid solutions, even if only to a limited extent.

Dr. Philip, in reply, said that the freezing-point curve for the system, acid anhydride—water, which had an intermediate summit at a temperature far above the freezing-points of the constituents, resembled those of the systems, mercury—sodium and α-naphthol—picric acid, studied by Kurnakoff and Kuriloff respectively.

He had not attempted to apply the Schroeder-Le Chatelier formula to his results, as the subject had been treated entirely from the experimental point of view.

The branches of the freezing-point curve, starting from the freezing-points of the components, although sometimes very nearly rectilinear, were, in the majority of cases, slightly concave to the concentration axis.

75. "*Isomeric partially Racemic Salts containing Quinquevalent Nitrogen.* Part XI. *Derivatives of* dl-*Methylhydrindamine and* dl-neo-*Methylhydrindamine. Isomeric Salts of the Type* $NR_1R_2H_3$." By G. Tattersall and F. S. Kipping.

The β-methyl-α-hydrindamine, obtained by reducing methylhydrindoxime, has been separated into the two externally compensated bases of which it is composed by the use of *d*-bromocamphorsulphonic acid, which forms with each of the *dl*-bases a partially racemic salt. The externally compensated base, which is present in the larger quantity, is called *methylhydrindamine*, the other being termed neo-*methylhydrindamine*.

Methylhydrindamine bromocamphorsulphonate,—

$$C_{10}H_{13}N,C_{10}H_{14}OBr\cdot SO_3H,H_2O,$$

crystallises from dilute alcohol in hydrated, rhombodial prisms, and, when dehydrated, melts at 160—165°. In dilute aqueous solution, this salt has a specific rotation $[\alpha]_D = +51\cdot5°$, and a molecular rotation $[M]_D = +235\cdot5°$. These values are abnormal, because, since the salt contains *dl*-base, its molecular rotation should be that of the bromocamphorsulphonic acid, namely, $[M]_D = +270°$.

The *benzoyl* derivative of methylhydrindamine melts at 151°; the *hydrochloride*, *sulphate*, and *picrate* are also described.

neo-*Methylhydrindamine bromocamphorsulphonate*,—

$$C_{10}H_{13}N,C_{10}H_{14}OBr\cdot SO_3H.$$

crystallises from alcohol in large, anhydrous, transparent prisms melting at 194°; its specific rotation in dilute aqueous solution is $[\alpha]_D = +58\cdot9°$, whence $[M]_D = +269\cdot5°$. This value is normal on the assumption that the salt is partially racemic, and this was proved to be the case.

The *benzoyl* derivative of *neo*-methylhydrindamine melts at 169°. The *hydrochloride*, *sulphate*, and *picrate* of the neo-base are also described.

dl Methylhydrindamine bromocamphorsulphonate is not resolved by ordinary fractional crystallisation, but when treated with a mixture of warm alcohol and ethyl acetate a precipitate of the salt of the *l*-base is obtained, the salt of the *d*-base remaining in solution.

l-*Methylhydrindamine bromocamphorsulphonate* separates from water in long, anhydrous needles, the original melting-point of which is 230°; its specific rotation in dilute aqueous solution is $[\alpha]_D = +45\cdot7°$, and molecular rotation $[M]_D = +209\cdot4°$. The free base is lævorotatory in dilute aqueous solution; its *hydrochloride*, which crystallises from water in needles or plates, has $[M_D] = +56°$.

d-*Methylhydrindamine bromocamphorsulphonate* is indistinguishable in appearance from the salt of the *l*-base; it has an original melting-point of 249°; its specific rotation is $[\alpha]_D = +71°$, and molecular rotation $[M]_D = +326°$. The free base is dextrorotatory in aqueous alcoholic solution.

The formation of isomeric partially racemic salts of the same type as those formed from hydrindamine and *d*-bromocamphorsulphonic acid having been expected, and such isomerides not having been found in the original mixture of salts, the question of their existence was solved by decomposing each of the pure partially racemic salts and regenerating each separately from its components. Crystallisation of the products failed to reveal the presence of any isomerides, so that it is concluded that isomeric partially racemic α- and β salts of methylhydrindamine and *neo*-methylhydrindamine do not exist.

Isomeric Salts of the Type $NR_1R_2H_3$.—On fractionally crystallising *l*-methylhydrindamine bromocamphorsulphonate, the melting-point of the first fraction after about twenty crystallisations rose to 236°, thus indicating that the original salt is a mixture. The pure salt (m. p. 236°) was then decomposed and regenerated from the same base and the same acid; fractional crystallisation of this product gave deposits with melting-points gradually falling from 236° to about 224°. The first and last fractions were found to differ also in specific rotation, the first fraction (*al*) having $[\alpha]_D = +47°$, $[M]_D = +216°$, whilst the last gave $[\alpha]_D = +41°$, $[M]_D = +188°$. The existence of isomeric salts derived from *l*-methylhydrindamine and *d*-bromocamphorsulphonic acid is thus proved.

The isomeric salt melting at 236° is called the *al* salt; the second isomeride, which is named the *βl*-salt, could not be obtained in a pure condition.

The *d*-methylhydrindamine bromocamphorsulphonate obtained by the resolution of the partially racemic salt was treated in the same way as the salt of the *l*-base, and regenerated from its component acid and base; the product was fractionally crystallised. The specific rotations in dilute aqueous solution and the melting points of the first and last fractions were found to be as follows:—

First fraction (*ad*).. ..	$[\alpha]_D = +73°$, $[M]_D = +334°$;	m. p. 262°.
Last fraction..	$[\alpha]_D = +67°$, $[M]_D = +307°$;	m. p. about 240°.

Here, again, the existence of isomerides, distinguished as the *ad*- and *βd*-salts, is established, but the former only was obtained in a pure condition.

The original *l*- and *d*-components are, therefore, mixtures, and consist of *al*- and *βl*-, and *ad*- and *βd*-salts respectively. If equal quantities of each are mixed before systematic crystallisation, the original partially racemic salt is obtained. If, however, equal weights of the *al*- and *ad*-salts are mixed, a partially racemic salt, different from the original one, is obtained:—

	M. p.	Crystalline form.	$[\alpha]_D$ in water.
Original partially racemic salt . ..	160—165°	Rhomboidal prisms	+51°
Synthetical partially racemic salt . ..	206°	Rectangular prisms	+60°

The original partially racemic salt consists of the four components, namely, *al*-, *βl*-, *ad*-, and *βd*-salts, and corresponds with the partially racemic β salt obtained from *dl*-hydrindamine and *d*-bromocamphorsulphonic acid.

76. "*The Action of Liquefied Ammonia on Chromic Chloride.*" By W. R. LANG and C. M. CARSON.

When liquefied ammonia acts on violet chromic chloride, a salmon-coloured powder is produced, from which water extracts two distinct compounds which are easily crystallisable *in vacuo*, and correspond in composition with the formulæ $Cr_2Cl_6,12NH_3,2H_2O$ and $Cr_2Cl_6,10NH_3$. The former substance is yellow, whilst the latter has the colour of cobalt nitrate. The salmon-coloured powder, when kept at 15°, yields both yellow and red crystals, but if heated to 110° it gives the red substance only. These compounds are completely decomposed at 180°.

77. "*Note on the Action of Methylamine on Chromic Chloride.*" By W. R. LANG and E. H. JOLLIFFE.

Methylamine acting on violet chromic chloride produces a pink powder very readily soluble in water, from which it can be crystallised with difficulty owing to the rapidity with which chromium hydroxide separates out. The composition of the crystals corresponds with the formula $Cr_2Cl_6,10CH_3\cdot NH_2$. The pink compound, when heated at 100°, yields a substance containing 8 mols. of ammonia; complete decomposition into chromic oxide occurs at 120°.

78. "*Cholesterol.*" (Preliminary note). By R. H. PICKARD and J. YATES.

Owing to the recent publication of the *Habilitationschrift* (Freiburg) of A. Windaus, bearing the above title, the authors wish to state that for over two years they have been investigating the constitution of cholesterol obtained from gallstones. The effects of nitric acid, fused potassium hydroxide, potassium chlorate and hydrochloric acid, and alkaline permanganate solution on cholesterol have been studied in turn. The results hitherto obtained show that the cholesterol is composed of a very stable, complex nucleus joined to a normal chain of some nineteen carbon atoms, inasmuch as arachidic acid, $C_{20}H_{40}O_2$, is one of the products of its oxidation. The

hydrocarbons obtained when cholesterol is treated with dehydrating agents and the action of alkalis on the halogen derivatives of cholesterol are also being investigated.

79. "*Hydrogen Cyanide in Fodder-plants.*" By J. C. Brünnich.

After the important discovery, by Messrs. Dunstan and Henry, of a glucoside "Dhurrin" (*Proc. Roy. Soc.*, 1902, lxx., 153) in the young plants of sorghum, which, on decomposition in presence of water, yields hydrogen cyanide, the author, on behalf of the Queensland Department of Agriculture, carried out a series of experiments in order to ascertain at what stages and conditions of growth the fodder-plants belonging to the sorghum family are most dangerous. Two varieties of sorghum, and also a variety of maize, were grown on unmanured and heavily manured plots, and analysed at various stages. The results show that sorghums should never be used as fodder in very young and immature stages of growth.

80. "*Sulphocampholenecarboxylic Acid.*" By A. W. Harvey and A. Lapworth.

When sulphocampholenecarboxylic acid (*Proc.*, 1902, xviii., 142) is oxidised with potassium permanganate, no oxalic acid is formed, and the product consists almost entirely of acids which cannot be removed from a strongly acidified aqueous solution by ether, ethyl acetate, or acetone, and is therefore probably a mixture of sulphonic acids. A minute quantity of a volatile fatty acid, perhaps acetic acid, was detected. When the oxidation product is carefully fused with potassium hydroxide, it yields a mixture of carboxylic acids, the main constituent being identified as $\alpha\alpha$-dimethylglutaric acid.

The *methyl* ester,—

$$CO_2Me\cdot C_9H_{14}Br\cdot SO_2\cdot O$$

(m. p. 192—193°), and the *ethyl* ester,—

$$CO_2Et\cdot C_9H_{14}Br\cdot SO_2\cdot O$$

(m. p. 101—102°), are very easily obtained from the sultonecarboxylic acid (*loc. cit.*) by Fischer's method. The carboxyl group is therefore attached to a hydrogenated carbon atom.

The above observations indicate (1) that in the formation of sulphocampholenecarboxylic acid from α-bromocamphor, scission has occurred between the carboxyl group and the trimethyl*cyclo*pentane nucleus, (2) that the acid does not contain the group $:C:CH\cdot CO_2H$, but probably $:C\cdot CH_2\cdot CO_2H$, (3) that it is most probably related to β- and not to α-campholenic acid in spite of its optical activity, which is perhaps due to the presence of the sulphonic group.

81. "*Optically Active Esters of β-Ketonic and β-Aldehydic Acids.* Part III. *Azo-derivatives of Menthyl Acetoacetate.*" By A. Lapworth.

Menthyl phenylazoacetoacetate,—

$$C_6H_5\cdot N_2\cdot CHAc\cdot CO_2\cdot C_{10}H_{19},$$

from menthyl acetoacetate and phenyldiazonium sulphate in presence of sodium acetate, forms large, transparent crystals melting at 76—77°. In a 1½ per cent solution in benzene, it has initially $[\alpha]_D = -21{\cdot}62$, and this rises after some days to a constant value $[\alpha]_D = -51{\cdot}52°$. The corresponding *p-tolylazo*-compound,—

$$C_6H_4Me\cdot N_2\cdot CHAc\cdot CO_2\cdot C_{10}H_{19},$$

melts at 86—87°, and in benzene has $[\alpha]_D = -11{\cdot}86°$ changing to $-61{\cdot}56°$; with phenylhydrazine, it yields *p-methylphenyl-4-azo-1-phenyl-3-methyl-5-pyrazolone*,—

$$\begin{array}{l} CMe{:}N\text{---}\text{---}\cdot NPh \\ | \qquad\qquad\quad | \\ CH(N_2\cdot C_6H_4Me)\cdot CO \end{array},$$

which forms yellow or orange needles melting at 136—137°.

Menthyl p-bromophenylazoacetoacetate,—

$$C_6H_4Br\cdot N_2\cdot CHAc\cdot CO_2\cdot C_{10}H_{19},$$

melts at 119—121°, and in benzene solution has $[\alpha]_D = -12{\cdot}84°$, changing to $-46{\cdot}88$; with phenylhydrazine, it gives rise to *4-bromophenylazo-1-phenyl-3-methyl-5-pyrazolone*,—

$$\begin{array}{l} CMe{:}N\text{---}\text{---}\cdot NPh \\ | \qquad\qquad\quad | \\ CH(N_2\cdot C_6H_4Br)\cdot CO \end{array},$$

which melts at 152—153°.

Menthyl p-chlorophenylazoacetoacetate,—

$$C_6H_4Cl\cdot N_2\cdot CHAc\cdot CO_2\cdot C_{10}H_{19},$$

melts at 103—105°, and in benzene has $[\alpha]_D = -15{\cdot}43°$ changing to $-55{\cdot}79°$; with phenylhydrazine, it gives *4-p-chlorophenylazo-1-phenyl-3-methyl-5-pyrazolone* melting at 141—142°.

The mutarotation of the above compounds is accelerated by traces of bases or acids. By the action of diazo-oxides on the esters, formazyl compounds are formed. The following have been isolated, but the colour of their solutions is too intense to admit of the determination of their rotatory power.

Menthyl pp'-dimethylphenylformazylcarboxylate,—

$$C_6H_4Me\cdot NH\cdot N{:}C(N_2C_6H_4Me)\cdot CO_2\cdot C_{10}H_{19},$$

forms dark red crystals with a blue reflex, and melts at 134—136°; *menthyl p-bromophenyl-p'-methylphenylformazylcarboxylate* melts at 149—151°; *menthyl p-chlorophenyl-p'-methylphenylformazylcarboxylate* melts at 145—147°.

The mutarotation of the azo-derivatives of menthyl acetoacetate is due to *iso*dynamic change in virtue of the lability of the α-hydrogen atom, and when this hydrogen atom is replaced by bromine the specific rotation becomes invariable. The α bromo-derivatives, which represent a new class of azo-compounds, were made (1) by direct bromination of the above esters, (2) by the interaction of a diazo oxide and menthyl α-bromoacetoacetate.

Menthyl phenylazo-α-bromoacetoacetate,—

$$C_6H_5\cdot N_2\cdot CBrAc\cdot CO_2\cdot C_{10}H_{19},$$

forms large, yellow crystals melting at 133—134°; it has $[\alpha]_D = -82{\cdot}45°$ in benzene. The corresponding *p-tolylazo*-compound, $C_6H_4Me\cdot N_2\cdot CBrAc\cdot CO_2\cdot C_{10}H_{19}$, melts at 155—156°, and has $[\alpha]_D = -85{\cdot}95°$. The *p-bromophenylazo*-compound, $C_6H_4Br\cdot N_2\cdot CBrAc\cdot CO_2\cdot C_{10}H_{19}$, melts at 155°, and has $[\alpha]_D = -73{\cdot}45°$; the *p-chlorophenylazo*-compound melts at 147—148°; it has $[\alpha]_D = -67{\cdot}61°$. The crystals of these four compounds exhibit anomalous dispersion of the optic axes.

The following note has been received since the meeting:—

82. "*The Chemical Reactions Involved in the Rusting of Iron.*" By W. R. Dunstan.

In a lecture delivered before the Royal Artillery Institution at Woolwich, the substance of which was published in the *Proceedings* of that Institution (1899, vol. xxvi., No. 5), and also in *Engineering*, June 1, 1900, the author gave a general account of the results of an investigation of the chemical process of rusting. This investigation, which was conducted with the co-operation of Dr. Jowett, was afterwards continued, and with the assistance of Mr. E. Goulding extended, especially to the atmospheric corrosion of iron and steel, and a further account of the results obtained was published in the Report (1900) of the Steel Rails Committee of the Board of Trade, of which the author was a member. Since then, the inquiry has been further extended, especially with reference to the atmospheric corrosion of pairs of metals, and to the elucidation of the general process. Various circumstances have, however, delayed the completion of the work, and the present summary of the results is published pending the preparation of a fuller account of the investigation.

It has been proved that whilst both liquid water and oxygen are necessary for the formation of rust, the presence of carbonic acid is not essential, although it may accelerate the action. The well-known effect of alkalis and alkaline salts in preventing the oxidation of iron has been hitherto attributed to the withdrawal of the carbonic acid. It has been found, however, that the phenomenon is not due to this cause, but to the establishment of conditions in which the production of hydrogen peroxide is inhibited.

When highly purified iron, containing mere traces of impurity, is left in contact with dry gases (oxygen, carbon dioxide, mixtures of oxygen and carbon dioxide), rusting does not take place. In the presence of the same gases and water vapour, no rusting occurs so long as a constant temperature (34° in the actual experiments) is maintained, but if the temperature is allowed to fluctuate, liquid water condenses on the surface of the iron and rust is produced. It is thus shown that pure iron is not oxidised in presence of gases and water-vapour only, but that the presence of liquid water is necessary for rusting to take place.

In another series of experiments, pieces of iron were left in contact with water saturated with a particular gas and with an atmosphere of the same gas above the solution. When hydrogen, carbon dioxide, or nitrogen which had been carefully freed from oxygen was employed, rusting did not occur, but if oxygen or a mixture of oxygen and carbon dioxide was used, oxidation took place. From these results, it is evident that for the formation of rust both oxygen and liquid water are required. In the experiments in which a mixture of oxygen and carbon dioxide was used, the results observed indicated that in this case a secondary action proceeds simultaneously.

In order to investigate the influence of solutions of various salts on the production of rust, small pieces of highly purified sheet iron were enclosed with the different solutions in sealed glass tubes, the space above the solution in each case being filled with pure oxygen. The following substances were found to prevent to a greater or less extent the formation of rust:—Sodium carbonate, ammonium carbonate, borax, disodium hydrogen phosphate, calcium hydroxide, ammonia, potassium dichromate, potassium ferrocyanide, chromic acid, sodium nitrite, and potassium carbonate. Rusting occurred in the presence of the following compounds:—Sodium chloride, potassium chlorate, ferrous sulphate, potassium ferricyanide, potassium nitrate, and sodium sulphate. The reagents which prevent the rusting of iron are those in presence of which decomposition of hydrogen peroxide takes place, and which are consequently inimical to its formation. There can be little doubt, therefore, that hydrogen peroxide plays an important part in the chemical process of rusting. By the direct action of hydrogen peroxide on metallic iron, a red basic ferric hydroxide, identical with ordinary rust, is rapidly produced, and it is found that in general those metals rust in air which are oxidised by hydrogen peroxide, whilst those metals which are not oxidised by hydrogen peroxide do not rust in air. Iron, zinc, and lead are examples of the first class, and the rusting of all these metals is stopped by contact with substances which prevent the formation of hydrogen peroxide. Copper, silver, and nickel are examples of the second class; these metals do not rust in air, and are not oxidised by hydrogen peroxide.

The analysis of a number of specimens of iron rust has shown that its composition may be represented by the formula $Fe_2O_2(OH)_2$.

The chemical reactions concerned in the process of rusting may therefore be represented by the following equations:—

$$Fe + O_2 + H_2O = FeO + H_2O_2.$$
$$2FeO + H_2O_2 = Fe_2O_2(OH)_2.$$

The presence of water in the liquid state is essential alike for the occurrence of rusting and for the formation of hydrogen peroxide.

In the case of certain metals, notably that of zinc, hydrogen peroxide can be detected during the process of rusting. It has not been possible, however, to detect with certainty the presence of hydrogen peroxide during the rusting of iron. This may be due to the fact, previously mentioned, that iron is very rapidly oxidised by hydrogen peroxide with formation of rust, so that under ordinary conditions the hydrogen peroxide is quickly destroyed.

The influence of certain other reactions on the process of rusting has been studied, and may be summarised as follows:—

I. The direct decomposition of water by metallic iron with liberation of hydrogen can take place only at a relatively high temperature, and is not affected by the presence of alkaline salts, such as sodium carbonate.

II. The action of aqueous carbonic acid on iron in the absence of oxygen results in the liberation of hydrogen, and formation of ferrous carbonate or bicarbonate. If oxygen is present, the ferrous salt subsequently undergoes oxidation, the rust obtained in this case containing a varying amount of carbonate.

III. Electrolytic action occurs when the iron is impure or when another metal is present. The electropositive metal suffers oxidation, and hydrogen gas is evolved. This action is not prevented by the presence of sodium carbonate.

PHYSICAL SOCIETY.

Ordinary Meeting, May 22nd, 1903.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

MR. J. STÖTTNER gave an Exhibition of Nernst Lamps, showing their development from the experimental form up to the most recent types.

Mr. Stöttner commenced by giving a short account of the history of the Nernst lamp, and explained briefly the principle of its action. The oxides used for the glowers are thoria, zirconia, and other rare earths thereto related, such as oxides of yttrium and cerium. A paste of these is formed, and small rods or tubes are pressed through a suitable nozzle. These are hardened and cut into small lengths, and practically the principal part of the lamp is finished. Several of these rods were passed round for the inspection of Fellows. The chief difficulty in the practical lamp is in the design of a durable automatic heater to heat the filament up to conducting point. A number of automatic arrangements which have been designed for disconnecting the heater were shown. Another important part of a Nernst lamp is the bolstering resistance, which in its final development consists of a thin iron wire sealed in a glass bulb filled with hydrogen gas. If a lamp is used without a bolstering resistance, as soon as a certain critical potential is reached the current increases, at first slowly and then quicker and quicker, the potential remaining constant, until the lamp burns itself out. This phenomenon was shown experimentally. Various forms of lamp were exhibited. One with two glowers and one heater overcomes the difficulty of thick glowers. A projection lamp was shown with three glowers in parallel requiring 300 watts. The glowers in this case were heated artificially. Mr. Stöttner also exhibited and described a pole-finder for use with lamps using direct current.

The CHAIRMAN said he would like to see details of the life and economy of these lamps under various conditions. The lamp was in its infancy, and probably even more satisfactory lamps would be forthcoming.

Mr. T. H. BLAKESLEY gave an Exhibition of a Diagram for Single-piece Lenses.

The properties of a single-piece lens are determined by four factors:—The two radii of curvature, the thickness of the lens, and the value of the refractive index of the material of which it is composed. In the case of a lens

of a particular thickness made of a material of definite refractive index, the variables reduce to two, namely, the ratios of the radii of curvature to the thickness of the lens. Any property of the lens requires a relation between these quantities. It is therefore possible, for any property, to draw a curve, with $\frac{r_1}{d}$ as ordinates and $\frac{r_2}{d}$ as abscissæ, such that any point on the curve represents a lens having that property. Mr. Blakesley has drawn curves representing several properties. Where two curves cut there is a point which gives a lens having the properties due to both curves. By means of such a diagram various lenses have been constructed, and three of them were shown at the meeting. Of these, one was equivalent to a Huyghens eye-piece and another to a collimator.

A paper on an "*Instrument for Measuring the Lateral Contraction of Tie-bars, and on the Determination of Poisson's Ratio*" was read by Mr. J. Morrow.

Practical methods for the determination of the ratio of lateral to linear strain in a tie-bar may be divided into three classes. First, those in which two coefficients of elasticity are determined and Poisson's ratio calculated; second, those depending on the deformation of the section of a beam; and lastly, methods by which the two strains are actually measured. Kirchoff and others have followed the first method, by experiments on combined twisting and bending; Cornu, Straubel, Mallock, and others the second, by examining the anti-clastic curvature produced in beams. Another method of the second type would be to find the displacements in the sides of a beam by measuring the lateral strains. Thus if f = maximum tensile stress, E = Young's Modulus, σ = Poisson's ratio, b and d the breadth and depth of beam, then σ is obtained from — angle turned through by side of beam $= \tan^{-1}\sigma\frac{f}{E}\cdot\frac{d}{b}$. The above methods depend on the practical accuracy of the theory of Elastic Materials. The experiments described in the paper belong to the third class, previous workers in which are Bauschinger and Stromeyer. The former used rather a complicated lever instrument, the displacements being measured by a mirror and telescope on each side of the specimen, and the latter employed an interference method. If α is the longitudinal strain produced by unit stress, and β the linear lateral strain, Poisson's ratio $= \sigma = \frac{\beta}{\alpha}$ and should be between 0 and $\frac{1}{2}$ for ordinary elastic bodies. The apparatus used in the research is described in the paper. It consists of two levers pivoted together. One end of each lever touches opposite ends of a diameter of the test-piece. The relative displacement of the other ends is measured optically. There are two mirrors, one fixed to one of the levers and the other resting by two needle-points on one lever and one point on the other. Two images of a scale are thus formed and brought together in a telescope. The relative motion of these images is a measure of the change in diameter or breadth of the specimen, the magnification used being about 2800. The instrument was tested on a bar of mild steel, and found to work consistently. A table of results is given, and from this the average values of σ are for mild steel 0·275, Sheffield spindle steel 0·276, wrought-iron 0·277, Muntz metal 0·341, and drawn copper 0·327. The specimens were not annealed, and were mostly about one inch in diameter. For the experiments on cast-iron, two series of specimens were carefully cast of material of good average quality. These were loaded several times in order to eliminate permanent set. The first series gave an average value $\sigma = 0{\cdot}246$ and the second $\sigma = 0{\cdot}252$. In order to determine whether permanent lateral set was produced in cast-iron by longitudinal stress, a bar one inch diameter which had not been previously loaded was carefully examined. It appeared to be perfectly elastic up to a load of half a ton, but afterwards set became evident. The results obtained are compared with those of Bauschinger and Stromeyer.

Prof. Everett said he had made determinations of Poisson's ratio by comparing the twist produced in a cylindrical rod by a torque, with the bend produced by an equal torque. The twist was always greater than the bend, and the ratio diminished by unity was Poisson's ratio, the material being supposed isotropic. This method was inapplicable to fibrous material; for instance, with wooden rods he had found the twist to be about five times the bend. Mr. Morrow's method had the advantage of being direct, and could be applied to fibrous materials as as well as to those which were isotropic. The experiments described in the paper were also on a far larger scale than had heretofore been employed. The mode of attachment of the mirror, which was a point of great importance in the experimental arrangements, seemed to be quite satisfactory.

Dr. Chree indicated several differences between the author's terminology and that usual in mathematical text-books. He also pointed out the expediency of explaining the units in which the values obtained for Young's modulus were expressed, and of adding the equivalent values in grammes weight per square centimetre. He referred to the fact that in the discussion of Wertheim's experiments on the value of Poisson's ratio given in Todhunter and Pearson's "History of Elasticity," it was pointed out that the materials employed seemed hardly to be isotropic, and that if this were the case the experiments could not be regarded as decisive. He also pointed out that more than one experimentalist had obtained results for cast-iron which indicated that, whilst it might be elastic, in the sense that strain disappeared on the removal of stress, it did not obey Hooke's law; and that if this were the case the application of the term Poisson's ratio to the material was not in accordance with mathematical usage. He dwelt on the importance of corroborative evidence in all cases that the materials dealt with were really elastic and isotropic.

The Chairman said it was difficult to assure oneself that the materials used were isotropic. The author's figures showed different values for Young's modulus for different specimens of the same material. He referred to the importance of stating the units employed, and the fact that the experiments had been carried out on an engineering scale.

Mr. Morrow said the units used in the paper were pounds and inches. His instrument was not dependent on the ordinary theory of elasticity. He pointed out that the values obtained for the Young's modulus of cast-iron depended upon the method employed, elongation and bending giving different results for the same specimen.

NOTICES OF BOOKS.

Technical Mycology; the Utilisation of Micro-organisms in the Arts and Manufactures. By Dr. Franz Lafar. Translated by Charles T. C. Salter. Vol. II. "Eumycetic Fermentation." Part I. With 68 Figures in the Text. London: Charles Griffin and Co., Ltd. 1903. Pp. 189.

In a publisher's note we are informed that, owing to repeated demands, it has been decided to publish the second volume of this work in parts, instead of awaiting the completion of the whole. Advance sheets have enabled the publishers to bring out the first part of this volume, and the concluding portion will follow as soon as the German proofs come to hand.

The present volume takes up the subject at Section X., which is on the general morphology and physiology of the eumycetes. The section contains four chapters, in which the author describes their general morphological

characteristics, the chemical composition of the cell membrane of eumycetes, &c., with some general remarks on the enzymes of eumycetes.

Section XI. is on fermentation by zygomycetes, and is devoted almost entirely to the mucors, fermentation by mucors, and the use of mucoreæ in the spirit industry.

Section XII. is on the form, structure, and chemical composition of the yeast cell, and especially in regard to the brewing of beer. The various kinds of yeasts are fully described, and their action in brewing dealt with.

The book is a valuable one, and bears full evidence of the enormous amount of work necessary for its compilation.

We think, however, that it would be considerably improved if the very numerous references to the work done by other observers had been omitted, either in part or altogether. We have not been able to find a single page which does not contain at least two of these references, while most pages contain eight, ten, or twelve, and even more; the effect is unfortunately to break up the continuity of the sentences and descriptions, and adds a good deal to the effort necessary to keep the mind concentrated on the subject under discussion.

Apart from this matter we have only praise for the book; it is well written, illustrated, and printed.

Notes on Metallurgical Analysis. By Nathaniel Wright Lord, E.M. Second Edition, Re-written and greatly Enlarged. Columbus, Ohio: Metallurgical Laboratory. 1903. Pp. 228.

The author's endeavour in preparing this, the second edition of this book, has been to extend its scope beyond the original idea, and to make it a reference book for metallurgical laboratories, as well as a text-book for students.

It is supposed, as a matter of course, that the student is familiar with all the ordinary details of chemical analysis and the routine of a laboratory, and with the help of the present volume he should be able to go through a course of metallurgical analysis without undue trouble.

All the ordinary metals are dealt with in turn, besides other materials in use in metallurgical operations, such as limestone, fuels, gases, slags, fire-clays, &c., and the recognised methods of assaying and analysing them are fully described. The book is well arranged, and contains a few useful tables at the end, but we are sorry to note that the general appearance is somewhat marred by careless printing in some parts.

Das Neue Institut für Metallhüttenwesen und Elektrometallurgie an der Königlichen Technischen Hochschule zu Aachen. Elektrische Messinstrumente. ("The New Institute for Smelting and Electro-metallurgy at the Royal Technical High School of Aachen. Electrical Measuring Instruments"). By Dr. H. Danneel. Halle-a-S.: Wilhelm Knapp. 1903.

This short account of the origin and development of the electro-metallurgical laboratory attached to the High School at Aachen, which has only very recently been completed, contains copious descriptions of the arrangements and contrivances of the laboratory. Much good work was done in the temporary laboratory, which was founded in the summer of 1898, and a brief report of the researches carried out under somewhat restricted and difficult circumstances prefaces the detailed description of the present building with its extensive and up-to-date appliances and conveniences. The amount of work which has emanated from the laboratory is sufficient to show the inspiring influence of the distinguished professor, Dr. Wilhelm Borchers, and his colleagues on the students, who have now every opportunity for profiting by one of the most perfect and complete laboratories of its kind in existence.

Der Stickstoff und Seine Wichtigsten Verbindungen. ("Nitrogen and its most Important Compounds"). By Dr. Leopold Spiegel. Braunschweig: Friedrich Viewig und Sohn. 1903.

The author of this work has endeavoured to do for nitrogen what Beilstein has already done for carbon—*i.e.*, collect in one volume all that is known of the element and its compounds, with special regard to the requirements of the original investigator. The chief desiderata are thus completeness and accuracy of detail, combined with the greatest possible convenience of arrangement for use as a book of reference. Considering the importance of nitrogen compounds in all branches of chemistry, physiological as well as inorganic and organic, the book's usefulness cannot be denied, and no one who refers to it for information on any point coming within its province is likely to be disappointed in not finding what he wants, or to be misled by inaccuracy. Some parts have necessarily been restricted to very little more than tabular abstracts, as, for instance, the sections on the alkaloids and protein substances, but no fault can be found with them, as far as they go, bearing in mind the fact that a text-book the size of the present volume could be written on these special branches of the subject. The literature references are taken up to the year 1900, and in some cases to a later date in the appendix, in which a few corrections and additions are made. Books such as this are likely to be of great use in leading to the elucidation of many problems of comparative chemistry, and of the relations of the inorganic compounds of the elements to one another.

Die Elektrochemie und die Metallurgie der für die Elektrochemie Wichtigen Metalle auf der Industrie- und Gewerbe-Ausstellung in Düsseldorf, 1902. ("Electrochemistry and the Metallurgy of the Metals of Importance in Electro-chemistry in the Trade and Industry Exhibition at Düsseldorf, 1902"). By H. Danneel. Halle-a-S.: Wilhelm Knapp. 1903.

This volume is a greatly enlarged edition of the report of the Düsseldorf Trade and Industry Exhibition, which appeared in the *Zeitschrift fur Elektrochemie.* It includes a brief description of the new electro-metallurgical Institute at Aachen, with a short account of some of the work which has been done there; in some cases this account follows the author's "Festschrift" of the same institute word for word. The most important exhibits of machinery and apparatus are fully described, with notes on various new processes for the dressing of ores, the preparation of metals by electro-chemical means, and the uses of aluminium, manganese, and the platinum metals. A list of awards of the gold, silver, and bronze medals in the various classes is added.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 18, May 4, 1903.

Compounds of Aluminium Chloride as Ferments.—G. Gustavson.—The author finds that, during the reaction between alcoholic chlorides and aromatic chlorides in presence of aluminium chloride, a substance is formed which is analogous to a ferment.

Action of Phosphorous Acid on Erythrite.—P. Carré.—Phosphorous acid behaves as a much less energetic dehydrating agent than phosphoric acid towards erythrite. The first product of this reaction is erythro-phosphorous

acid, $P(OH)_2OC_4H_9O_3$, and apparently this compound then fixes a further molecule of phosphorous acid, producing the body $P(OH)_2OCH_2CHOHCHOHCH_2OP(OH)_2$. The prolonged action of heat upon this latter substance gives rise to a volatile solid. Neutral phosphorous ether of erythran, $POHOC_4H_6O$, results from the reaction of the two phosphorous oxyhydriles on the secondary alcohol of erythran. This substance is immediately decomposed by water, giving the acid phosphorous ether of erythran, $P(OH)_2OC_4H_7O_2$, in which a single phosphorous oxyhydrile is contained. Erythrophosphorous acid and acid phosphorous ether of erythran cannot be isolated from their salts, because they are very unstable and are slowly saponified by cold water.

Organic Acids. — Œchsner de Coninck and M. Raynaud.—The authors examine the relative stability of the first acids of the formic series, and explain the mechanism of the decomposition of benzoic and phthalic acids by sulphuric acid.

Heat of Formation of certain Compounds of Barium.—M. Guntz.—The author finds the heat of oxidation of barium by first making a careful determination of the heat of solution of the metal in water. The mean value he obtains for this constant is +92·5 cal., and from this he calculates the heat of oxidation of barium to be +133·4 cal. He also determines the heat of formation of barium hydrate by decomposing a known weight of the hydrate by means of water. The number obtained is +37·5 cal. The heats of formation of the nitride and amide of barium are also found to be respectively +149·4 and 53·3 cal.

Chlorides of Chlorocinnamylidene and Bromocinnamylidene.—Ernest Charon and Edgar Dugoujon.—In a previous paper the authors showed that cinnamylidene chloride behaves as an acid chloride, and as such can be decomposed by water in the cold. They found that this particular property was due to the double liaison of the group $CHCl_2$. In their present research they further show that there is a distinct relation between the non-saturated character of the molecule and the stability of the group $CHCl_2$.

Transformation of Diphenylcarbonic and Monophenylsalicylic Ethers. — R. Fosse. — When phenyl carbonate, $CO_3(C_6H_5)_2$, is heated in presence of neutral sodium carbonate large bubbles of gas are formed, which rise to the surface of the liquid. These consist of carbonic anhydride and vapour of phenol. The reaction begins considerably below the boiling-point of phenylic ether, and it is due to the presence of the Na_2CO_3. The author obtained from the residue either phenylphenoxybenzoate, $C_6H_5—O.C_6H_4.CO_2.C_6H_5$, or phenoxybenzoic acid, $C_6H_5—O.C_6H_4.CO_2H$.

A New Diiodo-phenol.—P. Brenans.—The author investigates a fifth isomer of the diiodo-derivatives of phenol, $C_6H_3—OH—I_2$. 1 . 3 . 4. He obtains this by starting with the mono-iodo paranitraniline, $C_6H_3—NH_2—NO_2—I$. 1 . 4 . 2. The following succession of reactions take place:—(1) The diazo derivative of this iodo-nitraniline is decomposed by means of potassium iodide and changed into diiodo-nitrobenzene, $C_6H_3—NO_2—I_2$. 1 . 3 . 4. (2) The iodo-nitrobenzene is reduced to the corresponding diiodo-aniline, $C_6H_3—NH_2—I_2$. 1 . 3 . 4. (3) Finally, the diazo-sulphate of this base is heated in presence of water and transformed into diiodo-phenol, $C_6H_3—OH—I_2$. 1 . 3 . 4.

New Derived Bases of Pentoses.—E. Roux.—By reducing the oximes of arabinose and xylose by the same method as that previously used by the author for glucose, he obtains the two new bases arabinamine and xylamine.

Action of Alkalis on Glycerin. Application of this Reaction to the Estimation of Glycerin.—A. Buisine. —The author obtains, by the action of glycerin on potash lime, three different reactions, according as the temperature is between 220° and 250°, 250° and 280°, or 280° and 320°. The gas evolved during the process is pure hydrogen, the volume varying considerably in each case. These reactions can be applied to the estimation of glycerin, by measuring the volume of the evolved hydrogen. The author finds the third case, in which the reaction takes place about 320°, is the most satisfactory. The method is easily applied with simple apparatus. On the other hand, it is very sensitive—1 m.grm. of glycerin evolving about 7 c.m. of hydrogen; it is therefore very useful for estimating small quantities of glycerin.

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Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 24.

Preparation and Properties of a New Hydride of Silicon.—H. Moissan and S. Smiles.

Further Research on Liquid Hydride of Silicon, Si_2H_6.—H. Moissan and S. Smiles.

Some New Properties of Amorphous Silicon.—H. Moissan and S. Smiles.—The above three papers have been noticed already in these columns.

Research on Silicide of Calcium, $CaSi_2$. — H. Moissan and W. Dilthey.—Already noticed.

Examination of Silicide of Lithium.—H. Moissan.—Already noticed.

The Limits of Combustibility.—L. Pelet and P. Jomini.—When a combustible material is burnt in a confined space containing a definite amount of air the flame soon becomes extinguished. Analyses of the products of combustion show that the proportion of uncombined oxygen present is very variable. The oxygen left and that consumed up to the extinction of various combustible materials, determines the *limit of combustibility*. In the present paper the authors have endeavoured to determine on what factors the limits of combustibility depend in the case of various combustible materials. The following simple substances gave the results printed below when burnt in a confined space of 12 litres:—

	Oxygen consumed. Per cent.	Oxygen remaining. Per cent.
Sulphur, burnt in a dish 5 c.m. diameter	8·24	12·56
Hardwood charcoal	17·43	3 37
Hydrogen, flame 5 c.m. high	19·00	1·80
Magnesium	19·07	1·73
Yellow phosphorus	20·15	0·65

The following carbon compounds were treated in the same manner in a vessel of 7 litres capacity, and the results obtained were—

	Oxygen consumed. Per cent.	Oxygen remaining. Per cent.
Petroleum, in a lamp with a 65 m.m. wick	6·22	14·58
18 m.m. candles	6·68	14·12
Turpentine	8·82	11·98
Camphor	9·42	11·38
Naphthalene	10·10	10·70
Ethylic alcohol at 95°	10·98	9·82
Methylic alcohol	11·33	9·47
Benzene	12·28	8·52
Acetylene	13·86	6·94
Coal-gas	14·68	6·12
Ether	14·94	5·86
Sulphide of carbon	15·63	5·17

These results show that the limit of combustibility varies very considerably with the nature of the material. In the hope of finding the cause of these variations, the authors determined the temperatures of the flames by means of wires of platinum-gold alloys of different compositions. These measurements were only approximate, but they were able to obtain the following series, starting with the substance giving the coolest flame:—(1) Petroleum,

(2) candles, (3) sulphur, (4) alcohol, (5) benzene, (6) coal-gas, (7) carbon, (8) hydrogen, (9) phosphorus. From this it is seen that the higher the temperature of the flame the nearer the limit of combustibility approaches to 20·8 per cent of oxygen consumed. Finally, the authors sum up their results, that the limit of combustibility depends on—(*a*) The nature of the substance; (*b*) the temperature of the flame; (*c*) the amount of gaseous combustible introduced into the flame in a unit of time; and (*d*) the temperature of the surrounding air.

The Solubility of Paraformaldehyde in Solutions of Sulphite of Soda.—A. and L. Lumière and M. Seyewetz.—There are several drawbacks to the use of formaldehyde for the insolubilisation of gelatin, and the authors thought that, owing to its constancy of composition, trioxymethylene or paraformaldehyde, $(H.COH)_3$, might be used instead. For this reason they have examined its solubility in various saline solutions, and find that it is soluble in solutions of sulphite of soda; and that the maximum of solubility of paraformaldehyde is reached when its mixture with anhydrous sulphite of soda contains 30 to 60 per cent of the latter. Thus, we can obtain solutions containing from 25 to 29 per cent of trioxymethylene. The presence of paraformaldehyde in sufficient quantity (25 per cent) increases the solubility of the sulphite of soda, and enables up to about 55 per cent of this substance to be dissolved in water; the solution then contains 74 per cent of solid matter.

Some Properties of Compounds of the Form $R{-}CO{-}O{>}CH_2$ **and** $R{-}CO{-}O{>}CH_2$. — Marcel Descudé.—The author has examined the action of certain alcohols on chloroacetate of methylene, and finds that methylic alcohol gives dimethylformal and acetate of methyl. Ethylic alcohol gives similar results, as does also propylic alcohol. The alkaline alcoholates react on chloroacetate of methylene with extreme energy, giving rise to an abundant deposit of alkaline chloride. By operating with methylate of sodium, the author hoped to obtain the derivative $CH_3{-}COO{>}CH_2$, discovered by M. Friedel; but in this he was not successful.

The Hyposulphites of the Aromatic Amines.—A. Wahl.—Already noticed.

Constitution of the Aloines.—E. Léger.—Already noticed.

Anæstherin: a New Vegetable Cholesterin.—T. Klobb.—The author has extracted from the capitulum of the Roman camomile (*Anthemius nobilis*) a body which he considers ought to be placed among the phytosterines. The analysis of the benzoate of this body gives C = 83·02 and 82·90, H = 10·29 and 10·33; and its formula may be either $C_{28}H_{47}O.C_7H_5O$ or $C_{29}H_{49}O.C_7H_5O$. It occurs in pearly crystals, very soluble in benzene, sulphide of carbon, and chloroform, almost insoluble in cold alcohol, slightly soluble in boiling alcohol and hot petroleum ether. Boiling aqueous potash does not attack it. Anæstherin has several coloured reactions. Cold sulphuric acid gives an orange-red colouration; on evaporation with a little hydrochloric acid or Fe_2Cl_6 and taking up with chloroform, a violet colouration is obtained. By dissolving anæstherin in acetic anhydride, then adding sulphuric acid to the cooled solution, a permanganate-purple colour is obtained.

The Existence of Arsenic in the Animal Series.—G. Bertrand.—The author has examined a number of cetaceous marine birds, fishes, and animals, and finds all, from the higher vertebrates down to the sponges, contain small quantities of arsenic. Therefore the presence of this metalloid is not, as with other elements, at all characteristic of any group of creatures. It is found in all the tissues, and must be looked upon—with carbon, nitrogen, sulphur, or phosphorus—as a fundamental element of protoplasm.

Use of Cane-sugar Yeasts for the Fermentation of Cider.—Henri Alliot.—The author finds, as the result of a number of experiments, that cane sugar yeast is a saccharomycete of slight attenuation, and is quite fit to be used for the preparation of sweet ciders, as it has been shown that, as far as taste is concerned, the cider thus obtained is not different from ciders made with other yeasts.

A New Proof of the Cellular Resistance of the Saccharomycetes, and a New Application of this Property in Distilling Operations.—Henri Alliot.—A certain quantity of molasses is treated with its own weight of water and 4 grms. of sulphuric acid per litre, and placed in a retort. About a fifth of this is distilled over and added, a little at a time, at several hours' interval, to a pure culture of yeast in any sugary nutritive must as used in laboratories. The small initial amount only of the yeast requires to become acclimatised to the temperature (20—25°), and 1 litre is enough for a large distillery fermenting more than 1000 hectolitres of must every day.

MISCELLANEOUS.

Jubilee Presentation to Herr Ludwig Boltzmann.—On February 20th, 1904, Herr Ludwig Boltzmann will reach his sixtieth birthday. It is the intention to take this opportunity, as a token of universal respect and appreciation, of presenting to him a jubilee volume in the preparation of which scientific men throughout the whole world are invited to assist. Full particulars of the undertaking can be obtained from Dr. Stefan Meyer, Wien ix., Turkenstrasse 3.

City and Guilds of London Institute.—The Department of Technology of this Institute are about to hold an Exhibition of Practical Work executed by candidates at the Institute's technological and manual training examinations, 1903, in the North Gallery of the Imperial Institute. The exhibition will be opened on Thursday, June 11th, at 3 p.m. precisely, by the Most Hon. the Marquis of Londonderry, K.G., President of the Board of Education.

Livingstone College.—On Wednesday, June 10th, 1903, the Right Rev. the Lord Bishop of St. Albans will preside at a short meeting, to be held at 3.30 p.m. in the grounds of Livingstone College, on the occasion of the Commemoration Day proceedings. After the meeting the College will be open for inspection. Livingstone College has rendered great services in the past, not only to missionaries, but to all travellers in unhealthy regions, and it is hoped that the present opportunity will lead to much greater interest being taken in the work carried out under its auspices. Admission will be by ticket only, which may be obtained from the Principal, Livingstone College, Leyton, by those who are interested in the College and its work.

The Acetylation of Soluble Starch.—Fritz Pregl.—Franchimont was the first to show (*Comptes Rendus*, vol. lxxxix., p. 711) that the acetylation of cellulose by means of acetic anhydride and concentrated sulphuric acid is effected very easily, but that at the same time there is a rupture of the molecule. The author's experiments on the acetylation of soluble starch were carried out under the same conditions. Five grms. of dry soluble starch, prepared as described by Zulkowsky (*Berichte*, vol. xiii., p. 1395), were suspended in 50 grms. of acetic anhydride; to this was added a mixture of 2·5 c.c. of sulphuric acid and 7·5 c.c. of acetic acid; after forty hours, water was poured in, the precipitate is washed and purified by solution in acetic acid, and precipitation by alcohol. Analysis, as well as the titration of the acetyls, corresponds to a triacetate, $C_6H_7O_5(C_2H_3O)_3$. This derivative, saponified by alcoholic potash, regenerates the soluble starch with which we started, with all its properties. This soluble

starch answers to the formula $C_6H_{10}O_5$, and not to $3C_6H_{10}O_5 + H_2O$, given by Lyniewski (*Berichte*, vol. xxx., p. 2415). When we do the acetylation in the presence of more sulphuric acid, a product is formed soluble in hot alcohol, fusing at about 150—155°, with considerable swelling; its rotatory power $[\alpha]_D$ = about +149°. The saponification of the acetylised derivative gives a dextrine. —*Mon. f. Ch.*, vol. xxii., p. 1049.

Action of Zinc on the Alcoholic Solutions of the Halogenised Ketones.—I. Iotsitch.—By the action of zinc powder on the alcoholic solution of dibromacetophenone a crystalline product was obtained which appeared to be acetophenone. Bromhydrate of pulegon is transformed into menthone and pulegon by zinc powder. By treating butylchloral with zinc powder Zarnol has already obtained the chlorocrotonic and crotonic aldehydes. This reaction may be explained in several manners, and it was with the object of elucidating this point that the author has taken up the examination of the action of zinc on the β- and γ-halogen derivatives of the ketones and the aldehydes. Zinc powder reacts very vigorously on the alcoholic solution of trichlorethylideneacetophenone; a crystalline product is formed, fusible at 50—51°, which becomes yellow rapidly in the air, and is transformed into a liquid having a strong odour of the chloride of the acid. Attempts to prepare the acetic ether have not been successful. The elementary analysis points to a composition which would be that of the original compound, less 1 molecule of HCl; $C_6H_5 - CO - CH = CH - CCl_3$—HCl. The cryoscopic determination has given 209 for the molecular weight, instead of 213. The return is about 90 per cent. Zinc powder reacts with the same energy on trichlorethylideneacetone, giving a very unstable liquid product, resinifying in the air, and acquiring a strong odour of the chloride of the acid. Analysis points to a composition very close to $CH_3 - CO - CH = CH - CCl_3$—HCl. —*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 98.

MEETINGS FOR THE WEEK.

MONDAY, 8th.—Royal Institution, 5. General Monthly Meeting.
FRIDAY, 12th.—Physical, 5. "Some Experiments on Shadows in an Astigmatic Beam of Light," by Prof. S. P. Thompson. "The Positive Ionisation produced by Hot Platinum in Air at Low Pressures," by O. W. Richardson. "On a Method of Determining the Viscosity of Pitch-like Solids," by Prof. F. T. Trouton and E. S. Andrews.

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Re Pirie *v.* The Company and Others.—The Electro-Chemical Co. (1900), Ltd., 1901, E. 85.—By orders of Mr. Justice Farwell.

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THE CHEMICAL NEWS.

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MODERN VIEWS ON MATTER:

THE REALISATION OF A DREAM.*

By Sir WILLIAM CROOKES, F.R.S., &c.

FOR nearly a century men who devote themselves to science have been dreaming of atoms, molecules, ultra-mundane particles, and speculating as to the origin of matter: and now to day they have got so far as to admit the possibility of resolving the chemical elements into simpler forms of matter, or even of refining them altogether away into ethereal vibrations or electrical energy.

This dream has been essentially a British dream, and we have become speculative and imaginative to an audacious extent, almost belying our character of a purely practical nation. The notion of impenetrable mysteries has been dismissed. A mystery is a thing to be solved—"and Man alone can master the Impossible." There has been a vivid new start. Our physicists have re-modelled their views as to the constitution of matter and as to the complexity if not the actual decomposability of the chemical elements. To show how far we have been propelled on the strange new road, how dazzling are the wonders that waylay the researcher, we have but to recall—Matter in a fourth state, the genesis of the elements, the dissociation of the chemical elements, the existence of bodies smaller than atoms, the atomic nature of electricity, the perception of electrons, not to mention other dawning marvels far removed from the lines of thought usually associated with English chemistry.

The earliest definite suggestion in the last century of the possible compound nature of the elements occurs in a lecture delivered in 1809 by Sir Humphry Davy at the Royal Institution ("Works of Sir Humphry Davy," vol. viii., p. 325). In that memorable lecture he speculated on the existence of some substance common to all the metals, and he averred that "If such generalisations should be supported by facts, a new, a simple, and a grand philosophy would be the result. From the combination of different quantities of two or three species of ponderable matter we might conceive all the diversity of material substances to owe their constitution."

Again, in 1811, he said (*loc. cit.*, viii., 330):—"It will be useless to speculate upon the consequences of such an advancement in chemistry as that of the decomposition and composition of the metals. . . . It is the duty of a chemist to be bold in pursuit. He must not consider things as impracticable merely because they have not yet been effected. He must not regard them as unreasonable because they do not coincide with popular opinion. He must recollect how contrary knowledge sometimes is to what appears to be experience. . . . To inquire whether the metals be capable of being decomposed and composed is a grand object of true philosophy."

Davy first used the term "Radiant Matter" about 1809, but chiefly in connection with what is now called radiation. He also used the term in another sense, and the following passage in its clear forecast is prophetic of the modern electron (*loc. cit.*, vol. viii., p. 349):—"If particles of gases were made to move in free space with an almost infinitely great velocity—*i.e.*, to become radiant matter—they might produce the different species of rays, so distinguished by their peculiar effects."

In his lectures at the Royal Institution, in 1816, "On the General Properties of Matter," another prescient chemist, Faraday, used similar terms when he said—"If we conceive a change as far beyond vaporisation as that is above fluidity, and then take into account also the proportional increased extent of alteration as the changes rise, we shall, perhaps, if we can form any conception at all, not fall far short of radiant matter; and as in the last conversion many qualities were lost, so here also many more would disappear." Again, in one of his early lectures he strikes a forward note:—"At present we begin to feel impatient, and to wish for a new state of chemical elements. To decompose the metals, to reform them, and to realise the once absurd notion of transmutation, are the problems now given to the chemist for solution."

But Faraday was always remarkable for the boldness and originality with which he regarded generally accepted theories. In 1844 he said, "The view that physical chemistry necessarily takes of atoms is now very large and complicated; first many elementary atoms—next compound and complicated atoms. System within system, like the starry heavens, *may be right*—but may *be all wrong*."

A year later Faraday startled the world by a discovery to which he gave the title "On the Magnetisation of Light and the Illumination of the Magnetic Lines of Force." For fifty years this title was misunderstood and was attributed to enthusiasm or confused ideas. But to-day we begin to see the full significance of the Faraday dream.

It was not till 1896 that Zeeman showed a spectrum line could be acted on by a magnetic field. A spectrum line is caused by motion of the electron acting on the ether, which can only move and be moved by the electron. A magnetic field resolves this motion into other component motions, some slower others quicker, and thus causes a single line to split into others of greater and less refrangibility than the parent line.

In 1879, in a lecture I delivered before the British Association at Sheffield, it fell to my lot to revive "Radiant Matter" ("British Association Reports," Sheffield Meeting, 1879; CHEMICAL NEWS, vol. xl., p. 91; *Phil. Trans. Roy. Soc.*, 1879, Part I., p. 585; *Proc. Roy. Soc.*, 1880, No. 205, p. 469). I advanced the theory that in the phenomena of the vacuum tube at high exhaustions the particles constituting the cathode stream are not solid, nor liquid, nor gaseous, do not consist of atoms propelled through the tube and causing luminous, mechanic, or electric phenomena where they strike, "but that they consist of something much smaller than the atom,—fragments of matter, ultra-atomic corpuscles, minute things, very much smaller, very much lighter than atoms,—things which appear to be the foundation stones of which atoms are composed" (Sir O. Lodge, *Nature*, vol. lxvii., p. 451).

I further demonstrated that the physical properties of radiant matter are common to all matter at this low density—"Whether the gas originally under experiment be hydrogen, carbon dioxide, or atmospheric air, the phenomena of phosphorescence, shadows, magnetic deflection, &c., are identical." Here are my words written nearly a quarter of a century ago:—"We have actually touched the border land where matter and force seem to merge into one another—the shadowy realm between the known and unknown ("Matter is but a mode of motion," *Proc. Roy. Soc.*, No. 205, p. 472). I venture to think that the greatest scientific problems of the future will find their solution in this borderland, and even beyond; here, it seems to me, lie ultimate realities, subtle, far reaching, wonderful."

It was not till 1881 that J. J. Thomson established the basis of the electro-dynamic theory. In a very remarkable memoir in the *Philosophical Magazine* he explained the phosphorescence of glass under the influence of the cathode stream by the nearly abrupt changes in the magnetic field arising from the sudden stoppage of the cathode particles.

The now generally accepted view that our chemical elements have been formed from one primordial substance

* An Address delivered before the Congress of Applied Chemistry at Berlin, June 5, 1903.

was advocated in 1888 by me when President of the Chemical Society, in connection with a theory of the Genesis of the Elements (Pres. Address to Chem. Soc., March 28th, 1888). I spoke of "an infinite number of immeasurably small ultimate — or, rather, ultimatissimate — particles gradually accreting out of the formless mist, and moving with inconceivable velocity in all directions."

Pondering on some of the properties of the rare elements, I strove to show that the elementary atoms themselves might not be the same now as when first generated —that the primary motions which constitute the existence of the atom might slowly be changing, and even the secondary motions which produce all the effects we can observe—heat, chemic, electric, and so forth—might in a slight degree be affected; and I showed the probability that the atoms of the chemical elements were not eternal in existence, but shared with the rest of Creation the attributes of decay and death.

The same idea was expanded at a lecture I delivered at the Royal Institution in 1887, when it was suggested that the atomic weights were not invariable quantities.

I might quote Mr. Herbert Spencer, Sir Benjamin Brodie, Professor Graham, Sir George Stokes, Sir William Thomson (now Lord Kelvin), Sir Norman Lockyer, Dr. Gladstone, and many other English *savans* to show that the notion—not necessarily of the decomposability but at any rate of the complexity of our supposed elements—has long been "in the air" of science, waiting to take more definite development. Our minds are gradually getting accustomed to the idea of the genesis of the elements, and many of us are straining for the first glimpse of the resolution of the chemical atom. We are eager to enter the portal of the mysterious region too readily ticketed "Unknown and Unknowable."

Another phase of the Dream now demands attention. I come to the earlier glimpses of the electric theory of matter.

Passing over the vaguer speculations of Faraday and the more positive speculations of Sir William Thomson (now Lord Kelvin), one of the earliest definite statements of this theory is given in an article in the *Fortnightly Review* for June, 1875, by W. K. Clifford—a man who in common with other pioneers shared that "noblest misfortune of being born before his time." "There is great reason to believe," said Clifford, "that every material atom carries upon it a small electric current, *if it does not wholly consist of this current.*"

In 1886 when President of the Chemical Section of the British Association, in a speculation on the origin of matter, I drew a picture of the gradual formation of the chemical elements by the workings of three forms of energy—electricity, chemism, and temperature—on the "formless mist" (protyle*), wherein all matter was in the pre-atomic state—potential rather than actual. In this scheme the chemical elements owe their stability to their being the outcome of a struggle for existence—a Darwinian development by chemical evolution—a survival of the most stable. Those of lowest atomic weight would first be formed, then those of intermediate weight, and finally the elements having the highest atomic weights, such as thorium and uranium. I spoke of the "dissociation point" of the elements." "What comes after uranium?" I asked. And I answered back—"The result of the next step will be . . . the formation of . . . compounds the dissociation of which is not beyond the powers of our terrestrial sources of heat." A dream less than twenty years ago, but a dream which daily draws nearer to entire and vivid fulfilment. I will presently show you that radium, the next after uranium, does actually and spontaneously dissociate.

The idea of units or atoms of electricity—an idea hitherto floating intangibly like helium in the sun—can now be brought to earth and submitted to the test of experiment.* Faraday, W. Weber, Laurentz, Gauss, Zöllner, Hertz, Helmholtz, Johnstone Stoney, Sir Oliver Lodge, have all contributed to develope the idea—originally due to Weber—which took concrete form when Stoney showed that Faraday's law of electrolysis involved the existence of a definite charge of electricity associated with the ions of matter. This definite charge he called an electron. It was not till some time after the name had been given that electrons were found to be capable of existing separately.

In 1891, in my Inaugural Address as President of the Institution of Electrical Engineers,† I showed that the stream of cathode rays near the negative pole was always negatively electrified, the other contents of the tube being positively electrified, and I explained that "the division of the molecule into groups of electro-positive and electro-negative atoms is necessary for a consistent explanation of the genesis of the elements." In a vacuum tube the negative pole is the entrance and the positive pole the exit for electrons. Falling on a phosphorescent body, yttria, for instance,—a collection of Hertz molecular resonators —the electrons excite vibrations of, say, 550 billion times a second, producing ether waves of the approximate length of 5·75 ten-millionths of a millimetre, and occasioning in the eye the sensation of citron-coloured light. If, however, the electrons dash against a heavy metal, they produce ether waves of a far higher frequency than light, and are not continuous vibrations, but, according to Sir George Stokes, simple shocks or solitary impulses; more like discordant shouts as compared with musical notes.

During that Address an experiment was shown which went far to prove the dissociation of silver into electrons and positive atoms.‡ A silver pole was used, and near it in front was a sheet of mica with a hole in its centre. The vacuum was very high, and when the poles were connected with the coil, the silver being negative, electrons shot from it in all directions, and passing through the hole in the mica screen, formed a bright phosphorescent patch on the opposite side of the bulb. The action of the coil was continued for some hours, to volatilise a certain portion of the silver. Silver was seen to be deposited on the mica screen only in the immediate neighbourhood of the pole; the far end of the bulb, which had been glowing for hours from the impact of electrons, being free from silver deposit. Here, then, are two simultaneous actions. Electrons, or Radiant Matter shot from the negative pole, caused the glass against which they struck to glow with phosphorescent light. Simultaneously, the heavy positive ions of silver, freed from negative electrons, and under the influence of the electrical stress, likewise flew off and were deposited in the metallic state near the pole. The

* We require a word, analogous to protoplasm, to express the idea of the original primal matter existing before the evolution of the chemical elements. The word I venture to use is composed of πρό (*earlier than*) and ὕλη (*the stuff of which things are made*).

* "The equivalent weights of bodies are simply those quantities of them which contain equal quantities of electricity; . . . it being the ELECTRICITY which *determines* the equivalent number, *because* it determines the combining force. Or, if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalents to each other in their ordinary chemical action, have equal quantities of electricity naturally associated with them."—FARADAY'S "Experimental Researches in Electricity," par. 869, Jan., 1834.

"This definite quantity of electricity we shall call the molecular charge. If it were known it would be the most natural unit of electricity."—CLERK MAXWELL'S "Treatise on Electricity and Magnetism," First Edition, vol. i., 1873, p. 311.

"Nature presents us with a single definite quantity of electricity. . . . For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte, which is the same in all cases."—G. JOHNSTONE STONEY, "On the Physical Units of Nature," British Association Meeting, Section A, 1874.

"The same definite quantity of either positive or negative electricity moves always with each univalent ion, or with every unit of affinity of a multivalent ion."—HELMHOLTZ, Faraday Lecture, 1881.

"Every monad atom has associated with it a certain definite quantity of electricity; every dyad has twice this quantity associated with it; every triad three times as much, and so on."—O. LODGE, "On Electrolysis," *British Association Report*, 1885.

† "Electricity in Transitu: from Plenum to Vacuum" (*Journ. Inst. Electrical Engineers*, vol. xx., p. 10, January 15, 1891).

‡ In describing the experiment, one of fundamental importance, modern terms are employed.

ions of metal thus deposited in all cases showed positive electrification (*Proc. Roy. Soc.*, vol. lxix., p. 421).

In the years 1893-4-5 a sudden impulse was given to electric vacuum work by the publication in Germany of the remarkable results obtained by Lenard and Röntgen, who showed that the phenomena inside the vacuum tube were surpassed in interest by what took place outside. It is not too much to say that from this date that what had been a scientific conjecture became a sober reality.

One important advance in theoretic knowledge has been obtained by Dewar, the successor of Faraday in the classic laboratories of the Royal Institution. Soon after Röntgen's discovery Dewar found that the relative opacity to the Röntgen rays was in proportion to the atomic weights of bodies, and he was the first to apply this principle to settling a debated point in connection with argon. Argon is relatively more opaque to the Röntgen rays than either oxygen, nitrogen, or sodium, and from this Dewar inferred that the atomic weight of argon was twice its density relative to hydrogen. In the light of to-day's researches on the constitution of atoms, it is impossible to overestimate the importance of this discovery.

In 1896 Becquerel, pursuing the masterly work on phosphorescence inaugurated by his illustrious father, showed that the salts of uranium constantly emit emanations which have the power of penetrating opaque substances and of affecting a photographic plate in total darkness, and of discharging an electrometer. In some respects these emanations, known as Becquerel rays, behave like rays of light, but they also resemble Röntgen rays. Their real character has only recently been ascertained, and even now there is much that is obscure and provisional in the explanation of their constitution and action.

Following closely upon Becquerel's work came the brilliant researches of M. and Mdme. Curie, on the radioactivity of bodies accompanying uranium.

Hitherto I have been recounting isolated instances of scientific speculation with apparently little relation to one another. The existence of matter in an ultra-gaseous state; material particles smaller than atoms; the existence of electrical atoms or electrons; the constitution of Röntgen rays and their passage through opaque bodies; the emanations from uranium; the dissociation of the elements—all these isolated hypotheses are now focussed and welded into one harmonious theory by the discovery of Radium.

> "Often do the spirits
> Of great events stride on before the events,
> And in to-day already walks to-morrow."

No new discovery is ever made without its influence ramifying in all directions and explaining much that before had been mystifying. Certainly no discovery of modern times has had such wide-embracing consequences, and thrown such a flood of light on broad regions of hitherto inexplicable phenomena, as this discovery of M. and Mdme. Curie and M. Bémont, who patiently and laboriously plodded along a road bristling with difficulties almost insuperable to others who, like myself, have toiled in similar labyrinths of research. The crowning point of these labours is Radium.

Let me briefly recount some of the properties of Radium, and show how it reduces speculations and dreams, apparently impossible of proof, to a concrete form.

Radium is a metal of the calcium, strontium, and barium group. Its atomic weight according to C. Runge and J. Precht is probably about 258. In this case it occupies the third place below barium in my lemniscate spiral scheme of the elements, two unoccupied gaps intervening (*Proc. Roy. Soc.*, vol. lxiii , p. 408).

The spectrum of radium has several well-defined lines; these I have photographed and have also measured their wave-lengths. Two especially are strong and characteristic. One at wave-length 3649·71 and the other at wave-length 3814·58. These lines enable radium to be detected spectroscopically.

The most striking property of radium is its power to pour out torrents of emanations bearing a certain resemblance to Röntgen rays, but differing in important points.

The emanations of radium cause soda-glass to assume a violet colour, and they produce many chemical changes. Their physiological action is strong, a few milligrammes brought near the skin in a few hours producing a wound difficult to heal.

The emanations from radium are of three kinds. One set is the same as the cathode stream, now identified with free electrons—atoms of electricity projected into space apart from gross matter—identical with "matter in the fourth or ultra-gaseous state." Kelvin's "satellites," Thomson's "corpuscles" or "particles"; Lodge's "disembodied ionic charges, retaining individuality and identity." These electrons are neither ether-waves, nor a form of energy, but substance possessing inertia (probably electric). Liberated electrons are exceedingly penetrating. They will discharge an electroscope when the radium is ten feet or more away, and will affect a photographic plate, through five or six mm. of lead and several inches of wood or aluminium. They are not readily filtered out by cotton-wool; they do no not behave as a gas, *i.e.*, they have not properties dependent on intercollisions, mean free path, &c.; they act more like a fog or mist, are mobile and carried about by a current of air to which they give temporary conducting powers, clinging to positively electrified bodies and thereby losing mobility and diffusing on the walls of the containing vessel if left quiet.

Electrons are deviable in a magnetic field. They are shot from radium with a velocity of about one-tenth that of light, but are gradually obstructed by collisions with air atoms, so that some become much slowed, and then are what I formerly called loose and erratic particles, which diffuse about in the air, and give it temporary conducting powers. These can turn corners, can be concentrated by mica cones into a bundle and then produce phosphorescence.

Another set of emanations from radium are not affected by an ordinarily powerful magnetic field, and are incapable even of passing through thin material obstructions. These emanations have about one thousand times the energy of those radiated by the deflectable particles. They render air a conductor and act strongly on a photographic plate. Their mass is enormous in comparison with that of the electrons, and their velocity is probably as great when they leave the radium, but, in consequence of their greater mass, they are less deflected by the magnet, are easily obstructed by obstacles, and are sooner brought to rest by collisions with air atoms. The Hon. R. B. Strutt (*Phil. Trans. R. S.*, A, 1901, vol. cxcvi., p. 525) was the first to affirm that these non-deflectable rays are the positive ions moving in a stream from the radio-active body.

Rutherford has shown that these emanations are slightly affected in a very powerful magnetic field, but in an opposite direction to the negative electrons. They are therefore proved to be positively charged bodies moving with great velocity. For the first time Rutherford has measured their speed and mass, and he shows they are ions of matter moving with a speed of the order of that light.

There is also a third kind of emanation produced by radium. Besides the highly penetrating rays deflected by a magnet, there are very penetrating rays not at all affected by magnetism. These accompany the previous emanations, and are Röntgen rays—ether vibrations—produced as secondary phenomena by the sudden arrest of velocity of the electrons by solid matter, producing a series of Stokesian "pulses" or explosive ether waves shot into space.

Many lines of argument and research tending towards the same point give trustworthy data by which to calculate the masses and velocities of these different particles. I must deal with big figures, but big and little are relative, and are only of importance in relation to the limitations of

our senses. I will take as the standard the atom of hydrogen gas—the smallest material body hitherto recognised. The mass of an electron is 1/700th of an atom of hydrogen, or 3×10^{-26} grm. according to J. J. Thomson, and its velocity is 2×10^{9} centimetres per second, or two-thirds that of light. The kinetic energy per milligramme is 10^{17} ergs, about three and a-half million foot-tons. Becquerel has calculated that one square centimetre of radio active surface would radiate into space one gramme of matter in one billion years.

The positively electrified masses or ions are enormously great in comparison with the size of the electron. Sir Oliver Lodge illustrates it thus:—If we imagine an ordinary sized church to be an atom of hydrogen, the electrons constituting it will be represented by about 700 grains of sand each the size of an ordinary full-stop (350 positive and 350 negative) dashing in all directions inside, or, according to Lord Kelvin, rotating with inconceivable velocity. Put in another way; the sun's diameter is about one and a-half million kilometres, and that of the smallest planetoid about 24 kilometres. If an atom of hydrogen be magnified to the size of the sun, an electron will be about two-thirds the diameter of the planetoid.

The extreme minuteness and sparseness of the electrons in the atom account for their penetration. While the more massive ions are stopped by intercollisions in passing among atoms, so that they are almost completely arrested by the thinnest sheet of matter, electrons will pass almost unobstructed through ordinary opaque bodies.

The action of these emanations on phosphorescent screens is different. The electrons strongly affect a screen of barium platinocyanide, but only slightly one of Sidot's zinc sulphide. On the other hand, the heavy, massive, non-deflectable positive ions affect the zinc sulphide strongly, and the barium platinocyanide screen in a much less degree.

Both Röntgen rays and electrons act on a photographic plate and produce images of metal and other substances enclosed in wood and leather, and throw shadows of bodies on a barium platinocyanide screen. Electrons are much less penetrating than Röntgen rays, and will not, for instance, show easily the bones of the hand. A photograph of a closed case of instruments is taken by radium emanations in three days, and by Röntgen rays in three minutes. The resemblance between the two pictures is slight, and the differences great.

The power with which radium emanations are endowed of discharging electrified bodies is due to the ionisation of the gas through which they pass. This can be effected in many other ways; thus, ionisation is communicated to gases faintly by the splashing of water, by flames and red hot bodies, by ultra-violet light falling on negatively electrified metals, and strongly by the passage of Röntgen rays.

According to Sir Oliver Lodge's Electronic Theory of Matter, a chemical atom or ion has a few extra negative electrons in addition to the ordinary neutral atom, and if these negative electrons are removed it thereby becomes positively charged. The free electron portion of the atom is small in comparison with the main bulk, in the proportion in hydrogen of about 1 to 700. The negative charge consists of super-added or unbalanced electrons,—one, two, three, &c., according to the chemical valency of the body,—whereas the main bulk of the atom consists of paired groups, equal positive and negative. As soon as the excess electrons are removed, the rest of the atom, or ion, acts as a massive positively charged body, hanging tightly together. In a high vacuum the induction spark tears the components of a rarefied gas apart; the positively charged ions, having great comparative density are soon slowed down by collisions, while the electrons are driven from the negative pole with an enormous velocity depending on the initial electromotive force and the pressure of gas inside the tube, but approaching, at the highest exhaustions, half that of light.

After leaving the negative pole the electrons meet with a certain resistance, in a slight degree by physical collisions, but principally by reunion with the positive ions.

Since the discovery of radium and the identification of one set of its emanations with the cathode stream or radiant matter of the vacuum tube, speculation and experiment have gone hand in hand, and the two-fluid theory of electricity is gradually replaced by the original one-fluid theory of Franklin. On the two-fluid theory, the electrons constitute free negative electricity, and the rest of the chemical atom is charged positively, although a free positive electron is not known. It seems to me simpler to use the original one-fluid theory of Franklin, and to say that the electron is the atom or unit of electricity. Fleming uses the word "co electrons" to express the heavy positive ion a ter separation from the negative electron:—"We can no more," he says, "have anything which can be called electricity apart from corpuscles than we can have momentum apart from moving matter." A so-called negatively charged chemical atom is one having a surplus of electrons, the number depending on the valency, whilst a positive ion is one having a deficiency of electrons. Differences of electrical charge may thus be likened to debits and credits in one's banking account, the electrons acting as current coin of the realm. On this view only the electron exists; it is the atom of electricity, and the words positive and negative, signifying excess and defect of electrons, are only used for convenience of old-fashioned nomenclature.

The electron theory fits and luminously explains Ampère's idea that magnetism is due to a rotating current of electricity round each atom of iron; and following these definite views of the existence of free electrons, has arisen the electronic theory of Matter. It is recognised that electrons have the one property which has been regarded as inseparable from matter—nay, almost impossible to separate from our conception of matter,—I mean inertia. Now, in that remarkable paper of J. J. Thomson's published in 1881, he developed the idea of electric inertia (self-induction) as a reality due to a moving charge. The electron therefore appears only as apparent mass by reason of its electro-dynamic properties, and if we consider all forms of matter to be merely congeries of electrons, the inertia of matter would be explained without any material basis. On this view the electron would be the "protyle" of 1886, whose different groupings cause the Genesis of the Elements.

There is one more property of the emanations of radium to bring before your notice. I have shown that the electrons produce phosphorescence of a sensitive screen of barium platinocyanide, and the positive ions of radium produce phosphorescence of a screen of zinc blende.

If a few minute grains of radium salt fall on the zinc sulphide screen the surface is immediately dotted with brilliant specks of green light. In a dark room, under a microscope with a ⅔-inch objective, each luminous spot shows a dull centre surrounded by a diffused luminous halo. Outside the halo the dark surface of the screen scintillates with sparks of light. No two flashes succeed on the same spot, but are scattered over the surface, coming and going instantaneously, no movement of translation being seen.

If a solid piece of radium salt is brought near the screen, and the surface examined with a pocket lens magnifying about 20 diameters, scintillating spots are sparsely scattered over the surface. Bringing the radium nearer the screen the scintillations become more numerous and brighter, until when close together the flashes follow so quickly that the surface looks like a turbulent luminous sea. When the scintillating points are few there is no visible residual phosphorescence, and the successive sparks appear "atoms of intensest light," like stars on a black sky. What to the naked eye seems like a uniform "milky way," under the lens becomes a multitude of stellar points, flashing over the whole surface.

"Polonium" basic nitrate, actinium, and radio-active platinum produce a similar effect on the screen, but the

scintillations are fewer. In a vacuum the scintillations are as bright as in air, and being due to inter-atomic motion they are not affected by extremes of low temperature: in liquid hydrogen they are as brilliant as at the ordinary temperature.

A convenient way to show these scintillations is to fit the blende screen at the end of a brass tube with a speck of radium salt in front about a millimetre off, and to have a lens at the other end. I propose to call this little instrument the "Spinthariscope," from the Greek word σπινθαρίς,* a scintillation.

It is difficult to estimate the number of flashes of light per second. With the radium about five centimetres off the screen the flashes are barely detectable, not more than one or two per second. As the distance of the radium diminishes, the flashes become more frequent, until at one or two centims. they are too numerous to count, although it is evident this is not of an order of magnitude inconceivably great.

Practically the whole of the luminosity on the blende screen, whether due to radium or "polonium," is occasioned by emanations which will not penetrate card. These are the emanations which cause the scintillations, and the reason why they are distinct on the blende and feeble on the platinocyanide screen, is that with the latter the sparks are seen on a luminous ground of general phosphorescence which renders the eye less able to see the scintillations.

It is probable that in these phenomena we actually witness the bombardment of the screen by the positive ions hurled off by radium with a velocity of the order of that of light. Each particle is rendered apparent only by the enormous extent of lateral disturbance produced by its impact on the sensitive surface, just as individual drops of rain falling on a still pool are not seen as much, but by reason of the splash they make on impact, and the ripples and waves they produce in ever-widening circles.

Indulging in a "Scientific Use of the Imagination," and pushing the hypothesis of the electronic constitution of Matter to what I consider its logical limit, we may be, in fact, witnessing a spontaneous dissociation of radium—and we begin to doubt the permanent stability of matter. The chemical atom may be actually suffering a katabolic transformation; but at so slow a rate that supposing a million atoms fly off every second, it would take a century for weight to diminish by one milligramme.

It must never be forgotten that theories are only useful so long as they admit of the harmonious correlation of facts into a reasonable system. Directly a fact refuses to be pigeon-holed and will not be explained on theoretic grounds, the theory must go, or it must be revised to admit the new fact. The Nineteenth century saw the birth of new views of atoms, electricity, and ether. Our views to-day of the constitution of matter may appear satisfactory to us, but how will it be at the close of the Twentieth century? Are we not incessantly learning the lesson that our researches have only a provisional value? A hundred years hence shall we acquiesce in the resolution of the material universe into a swarm of rushing electrons?

This fatal quality of atomic dissociation appears to be universal and operates whenever we brush a piece of glass with silk; it works in the sunshine and raindrops, and in the lightnings and flame; it prevails in the waterfall and the stormy sea. And although the whole range of human experience is all too short to afford a parallax whereby the date of the extinction of Matter can be calculated, Protyle, the "formless mist," once again may reign supreme, and the hour hand of eternity will have completed one revolution.

* Ενθ ἑκ νηὸς ὄρουσεν ἄναξ, ἑκάεργος Ἀπόλλων,
ἀστέρι εἰδόμενος, μέσῳ ἡματὶ τοῦ δ' ἀπὸ πολλαὶ
σπινθαρίδες πωτῶντο, σέλας δ' εἰς οὐρανὸν ἵκεν'.

(Here from the ship leaped the far-darting Lord Apollo, like a star at midday, while from him flitted scintillations of fire, and the brilliancy reached to heaven.—Homer's *Hymn to Apollo*, lines 440—442

A NEW CLASS OF PERURANATES.

By. J. ALOY.

When we add peroxide of hydrogen to a soluble salt of uranium, a white precipitate of peruranic hydrate is produced. But if we operate in the presence of alkali we obtain, on the contrary, a solution which deposits yellow crystals of peruranates spontaneously, or better in the presence of alcohol. The composition of these different compounds is being still vigorously discussed. While most writers give peruranic oxide the formula UO_4, Fairley, who discovered it, looks upon it as a mixed oxide, $UO_6(UO_3)_2$ (*Chem. Soc.*, vol. i., p. 127). As for the yellow peruranates, according to Melikoff and Pissarjewski (*Journ. Soc. Phys. Chim. R.*, 1898, vol. xxx., p. 103), they result from the union of UO_4 with the peroxides, such as Na_2O_2.

The solution which gives rise to the formation of the peruranates always has a more or less pronounced red colour; Fairley attributed this colouration to the formation of a red peroxidised salt. In fact, by using small quantities of soda, under conditions which he did not fully explain, he obtained a red oil, which he regarded as a mixed salt of uranium and sodium. He was not able to prepare the corresponding potassium salt.

In reality, the red oil spoken of by Fairley is a solution of a solid peruranate that I have succeeded in isolating. I showed, firstly, that by substituting alkaline carbonates for the alkalis, it is very easy to produce red solutions of the peruranates. This reaction even forms one of the best characteristic tests for salts of uranium, and can be used also for detecting the presence of peroxide of hydrogen (Aloy, *Bull. Soc. Chim.*, Series 3, vol. xxvii., p. 734). Following this, I prepared the solid peruranates by several methods. I will describe the two following methods, as being easy of application:—

1. A solution of nitrate of uranium is treated with peroxide of hydrogen in sufficient quantity to precipitate the whole of the metal; wash by decantation and add some solid alkaline carbonate. In this manner we obtain a red solution which, when treated with ordinary alcohol, gives a red oil analogous to that described by Fairley. The excess of carbonate is removed by treatment with dilute methylic alcohol, which separates the peruranate in the crystalline form. It is always difficult, however, to remove the last traces of the carbonate by this method.

2. To obtain the pure salt it is preferable to proceed in the following manner:—The peruranic hydrate is suspended in peroxide of hydrogen, and a small quantity of alcohol added. To this mixture the alkali, free from carbonate, is added, while stirring continuously. First of all, a very abundant precipitate is formed; this disappears gradually, and there remains at the bottom of the beaker a red substance, which adheres to the sides very persistently. The beaker is turned over to separate the solid from the solution, and then treated several times with pure methylic alcohol. The peruranate becomes detached from the sides and takes a crystalline form.

This method is applicable to the salts of potassium and sodium; it is not so successful in the case of barium.

The peruranates formed in this manner are red, crystalline, very heavy solids. They are rather unstable and lose oxygen slowly at the ordinary temperature; at 100° the decomposition is rapid and complete.

They are destroyed by water, forming insoluble uranates.

Hydrochloric acid decomposes them with the evolution of chlorine; by the action of dilute nitric acid peruranic hydrate is formed, without any evolution of gas.

For the analysis of these compounds I made use of the method employed for the analysis of the yellow peruranates.

The uranium was estimated in the state of U_3O_8, the potassium in the state of chloroplatinate, and the water directly. To estimate the oxygen two methods are ap-

plicable. We can measure the volume of the gas resulting from the decomposition of the salt, and calculate it as uranic acid, UO_3. Or else, as has been recommended by Zimmermann (*Lieb. Ann. Ch.*, vol. ccxxxii., p. 273), reduce the salt by means of iodide of potassium and hydrochloric acid, and estimate the iodine set free by means of hyposulphite.

I prefer the former method, which is generally used in the analysis of peroxidised compounds.

The potassium salt answers to the formula $UO_5K_2.3H_2O$.

	Calculated.	Found.	
UO_3	63·72	63·58	63·70
O_2	7·08	6·87	6·95
K_2	17·25	17·33	17·35
$3H_2O$	11·95	12·00	12·11
	100·00		

The sodium salt has the composition $UO_5Na_2\,5H_2O$.

	Calculated.	Found.	
UO_3	63·13	63·20	63·31
O_2	7·01	6·85	6·78
Na_2	10·08	10·12	10·30
$5H_2O$	19·75	20·10	20·04
	100·00		

Thus, there are two quite distinct classes of peruranates; the red peruranate that I have described, and which corresponds to the acid $UO_4.H_2O$, and the yellow salt, $UO_4(M_2O_2)_2$, discovered by Fairley.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 8.

THE SEPARATION AND ESTIMATION OF ANTIMONY BY THE ELECTROLYTIC METHOD.

By A. HOLLARD.

THE electrolytic estimation of antimony in solution in sulphydrate of sodium, which was described by Classen as being particularly suitable in the presence of tin and arsenic, since these elements are not deposited on the cathode with the antimony, is really open to certain objections pointed out already by Ost and Klapproth (*Zeit. f. Angew. Chem.*, 1900, p. 827), and by the present author (*Comptes Rendus*, 1896, vol. cxxiii., p. 1064; *Ann. de Chim. Analytique*, 1897, p. 242; *Bull. Soc. Chim.*, 1900, vol. xxiii., p. 291).

We will summarise these objections, and will describe a modification we have applied to Classen's method, which modification constitutes an excellent means of separation and estimation.

We have shown already that the use of concentrated sulphydrate of sodium, as described by Classen, offers serious difficulties; at the same time as the antimony, it dissolves appreciable quantities of copper (3 to 4 m.grms. per 100 c.c.), a metal which accompanies antimony very frequently; this copper is deposited on the cathode at the same time as the antimony.

We have got over this difficulty by transforming the copper into the state of complex cyanide ions, not susceptible of being deposited on the cathode; for this purpose it sufficed to add cyanide of potassium to the solution of sulphydrate of sodium.

On the other hand, Ost and Klapproth observed that the increasing amount of polysulphides formed round the anode during the course of the electrolysis, by the use of Classen's concentrated sulphydrate, passes by diffusion to the cathode, where it is able to dissolve the antimony already deposited. They proposed to arrest this diffusion by means of a diaphragm. The addition of cyanide of potassium to which we have just alluded prevents these difficulties occurring, and renders the use of a diaphragm superfluous.

The following is the method of procedure:—The antimony in the state of sulphide, or as oxide made slightly alkaline by the addition of soda, is dissolved in a mixture of 200 c.c. of saturated sulphydrate of sodium (density = 1·220 to 1·225), and 40 c.c. of an aqueous solution of cyanide of potassium at 20 per cent.

The electrodes are plunged completely into this solution, which occupies a volume of 240 c.c. These electrodes are the same as those we have already described (*Bull. Soc. Chim.*, 1900, vol. xxiii., p. 291), except that the truncated conical electrode which serves as the cathode is made of platinum gauze instead of platinum foil. The current should be about 0·1 ampère.

The presence of tin does not interfere with the reaction, provided there is not more than 1 grm. present.

Neither does the presence of copper matter, so long as there is not more than 0·05 grm. present. Further, it is always easy to keep below this proportion; it suffices to take up the compounds of copper and antimony by means of sulphydrate of sodium without cyanide, and to add the cyanide to the filtered sulphydrate solution.

The presence of arsenic does not interfere so long as it is in the state of arsenic acid, as shown by experiments 10, 11, and 12; further, Classen has pointed this out.

Preparation of the Concentrated Sulphydrate of Sodium.—The preparation of this reagent offers some difficulty; we shall therefore describe it in some detail.

A solution of soda is prepared of 1·3 density quite free from arsenic.* Five hundred c.c. are placed in a flask of at least 1·25 litres capacity, into which a wide tube is plunged. By means of this tube a strong current of sulphuretted hydrogen is passed through the soda, and this must not be stopped during the whole time of saturation; under these conditions the reaction is sufficiently lively to cause a slight disengagement of heat, which interferes with the crystallisation of the neutral sulphide of sodium, which is slightly soluble, and which would block up the tube if it was precipitated. The current of sulphuretted hydrogen is stopped when the level of the liquid, which rises continuously during saturation, rises no longer. At this point the remaining 500 c.c. of soda (density 1·3) are added to the sulphydrate formed; there is immediately an abundant crystalline precipitate of sulphide of sodium, which is re-dissolved with the help of a vigorous current of sulphuretted hydrogen, which must be kept up until the volume of the liquid no longer increases.

The solution of sulphydrate of sodium is transferred to a large porcelain crucible; it is boiled for twenty minutes, provided no crystalline skin is formed on the surface of the liquid before that time, in which case the flame must be withdrawn immediately.

The hot liquid is filtered through a double folded filter, which retains the insoluble impurities; it is then allowed to cool, and water is added to make the density 1·220 to 1·225.

The liquid should be kept away from the light in small flasks, well-filled, and tightly corked. In this manner the formation of polysulphides is prevented.

We can also prepare this sulphydrate of sodium by one single saturation instead of two; but in that case not more than 500 c.c. of soda must be used at a time, for fear of producing crystals of sulphide of sodium which would block up the tube. The saturation by sulphuretted hydrogen in two operations—which is also recommended by Classen—is more advantageous, as it enables us, in a relatively short time, to obtain large quantities of the sulphydrate.

* It is necessary, therefore, to guard against using soda-lime resulting from the preparation of sulphate of soda, as this salt is prepared by means of sulphuric acid generally very rich in arsenic. Alcoholic soda or even commercial ammoniacal soda-lye will do very well.

Experimental Results.

		Quantities weighed. Grm.	Sb deposited. Grm.
1.	Sb	0·1492	0·1504
2.	Sb	0·2000	0·2027
3.	Sb	0·1483	0·1543
4.	Sb	0·1500	0·1438
5.	Sb	0·4990	0·4990
	Sn	1 0000	—
6.	Sb	0·1473	0·1478
	Sn	0·3000	—
7.	Sb	0 1011	0·1008
	Sn	1·0000	—
	Cu	0·5000	—
8.	Sb	0·1490	0·1456
	Sn	0 1000	—
	Cu	0·0500	—
9.	Sb	0·2001	0·2024
	Sn	1·0000	—
	Cu	0·0500	—

Influence of Arsenic According to its Degree of Oxidation.

(As_V signifies:—Arsenic in the state of arsenic acid.
As_{III} „ „ „ „ arsenious acid).

10.	Sb	0·0988	0·0982
	Cu	0·0500	—
	As_V	0·1000	—
11.	Sb	0·1489	0·1511
	Sn	1·0000	—
	Cu	0·0500	—
	As_V	0·1000	—
12.	Sb	0·1482	0·1561
	Sn	1·0000	—
	Cu	0·0500	—
	As_{III}	0·1000	—

In all these experiments the antimony, tin, and copper were attacked with nitric acid, evaporated to dryness, and the residue, made alkaline with soda, was taken up with the mixture of sulphydrate and cyanide. In experiment No. 7 only, the antimony, tin, and copper were in the form of sulphides.—*Bull. Soc. Chim.*, Series 3, vol. xxix., p. 262.

ON THE CONSTITUTION OF THE ELECTROLYTIC PEROXIDES OF LEAD, NICKEL, AND BISMUTH.

By A. HOLLARD

Lead.

IT has always been admitted, up to the present time, that the peroxide of lead which is deposited on the anode in a saline solution of lead through which an electric current is passed, is the binoxide of lead, PbO_2, and the figure 0·866, which represents the proportion $\frac{Pb}{PbO_2}$ of the molecular weights of the lead and of the binoxide, has been given as the analytic factor for converting the weight of the peroxide deposited into the corresponding weight of lead. Contrary to this statement we have found:—(1) That the factor 0·866 is too high, and that besides PbO_2, superoxides more highly oxidised than PbO_2 are also deposited at the anode; (2) that the proportion of these superoxides is the greater as the concentration of the lead in the bath is less.

We have worked on a series of solutions of nitrate of lead (obtained from very pure lead from different sources), all of the same volume (300 c.c.), and all containing the same excess of nitric acid (12 c.c. of acid at 36°). The amounts of lead contained in these solutions varied in each case, from a few m.grms. up to 10 grms. The electrodes we used were made of platinum.

We have already described them (*Bull. Soc. Chim.*, vol. xxiii., p. 291) as far as their size and shape are concerned, but in the present instance the truncated conical electrode A, which serves as the anode, is made of platinum gauze instead of platinum foil. To obtain perfectly adherent and compact deposits on the anode, which is particularly difficult when dealing with large quantities of lead, we made use of a *platinised* platinum gauze,* and we added a large amount of nitrate of copper (equal to 10 grms. of copper) to the bath.†

This nitrate deposits only a portion of its copper on the cathode, while the whole of the lead is deposited on the anode in the state of peroxide. None of the deposits of peroxide were weighed until after having been washed,‡ and then dried in an oven heated gradually up to 200°.

In the following table we give the means of our results. Column I. gives the weight of lead present in the different baths; Column II. gives the corresponding analytic factors $\left(\frac{\text{weight of lead}}{\text{weight of peroxide}}\right)$:—

I.	II.	III.
0·0106	0·740	0·740
0 02	0·764	0·764
0·03	0 790	0·790
0·05	0 802	0·802
0·07	0·824	0·824
0·1	0·838	0·835
0·2	0 842	0·843
0·5	0·851	0·850
1·0	0·852	0·852
2 0	0·8545	0·8545
2·5	0·855	0·855
3·0	0·856	0·856
5·0	0·859	0·859
10·0	0·861	0·861

If we plot these results on a curve, taking the figures of Column I. as abscissæ, and those of Column II. as ordinates, it will be seen that at first the curve rises very rapidly up to a point corresponding to 0·1 grm. of lead; then it is inflected strongly but regularly to a point corresponding to 0·6 grm.; the remainder of the curve is almost a straight line, or at least of a very slight curvature, and it tends to reach the point 0·866 without, however, being able to attain it.

In column III. we have given the actual points through which the regular curve passes. It will be observed, if the curve be made, that it passes exactly through all the points found experimentally, with the exception of those corresponding to the abscissæ 0·1, 0·2, and 0·5 grm.

Interpretation of Results.—In the electrolysis of all these solutions the total quantity of oxygen carried to the anode during the whole course of the electrolysis is greater than that required for the exclusive formation of the binoxide, PbO_2. This excess of oxygen, which with high concentrations of lead is *nil*, or at least very slight at the commencement of the electrolysis, becomes considerable in the case of low concentrations; as a matter of fact, the proportion of oxygen is the same in all the solutions whether rich or poor in lead, and it remains constant during the whole course of the electrolysis. Thus we see how it is possible for higher oxides, more oxidised than PbO_2, to be formed, and how the proportion of these superoxides increases with the dilution.

The factors corresponding to the lowest concentrations show us that these superoxides are of a very high order.

* Platinum gauze has already a large surface. *Platinising* consists of covering the gauze electrolytically with a layer of platinum in a strongly acid (hydrochloric) bath, containing also oxalate of ammonia. In this manner we obtain a surface, the roughness of which is specially capable of retaining large quantities of peroxide of lead.

† The fortunate influence of nitrate of copper on the compactness of the peroxide of lead has been pointed out by Dandurand.

‡ To do this without detaching the electrodes, they were first plunged for an instant into a vessel of distilled water, then, *while still passing the current*, into a second vessel, also containing distilled water, for a quarter of an hour.

We are not able to say yet that we have to deal with only one highly oxidised superoxide, of which the proportion should increase gradually as the solution becomes more dilute, or whether we have to do with a series of superoxides, the more oxidised as they are formed at greater dilutions.

According to the preceding remarks, if we take a sufficiently concentrated solution of lead, there is no excess of oxygen at the commencement of the electrolysis, and a layer of PoO_2 is formed first; then, when the concentration has become diminished sufficiently, on account of the deposition of peroxide of lead at the anode, the oxygen, of which the concentration remains constant, is found to be in excess with regard to the lead; consequently, superoxides are formed in quantities that increase as the concentration of the lead diminishes.

This explanation is the one which appears to us to be the most reasonable, but it will be advisable to confirm it by control experiments. Two of these control experiments are immediately apparent:—

1. Make a deposit of peroxide in a solution kept at a high concentration, and see whether the deposit consists of pure PbO_2.

2. Make a deposit of peroxide in very dilute solution (a few m.grms. only of lead per 300 c.c.), keeping the concentration constant, until a thick layer of peroxide has been formed, and see whether this peroxide has the constitution of a superoxide as highly oxidised as that shown by the curve at a similar concentration.

But what remains, independently of this explanation, is the grave error that has been committed, up to the present, in electrolytic analysis by admitting that electrolytic peroxide of lead is PoO_2, and that the factor is 0·866. The curve and the tables will enable us in the future to obtain factors corresponding to a large number of concentrations of lead.

Nickel.

Lead is not the only metal which forms superoxides of a high order by electrolysis. Nickel, in alkaline solution of pyrophosphate treated with chromic acid, gave a peroxide—with a concentration of 0 05 grm. of nickel per 300 c.c., the bath being at a temperature of 70°—which, dried at 120°, corresponded to the constitution NiO_4, and which did not vary in weight when heated as high as from 120° to 170°. The current, which was of 0·1 ampère, was passed through the bath for fifty-four hours.*

This peroxide is very difficult to obtain. The most highly oxidised oxide of nickel yet known answers to the formula Ni_2O_3.

Bismuth.

Bismuth gave a deposit at the anode which, when dried at 130°, corresponded to the formula Bi_2O_7 in a concentration of 0·05 grm. of bismuth per 300 c.c. of bath.

The bismuth was in the form of sulphate, in the presence of 20 c.c. of nitric acid at 36° in excess, and 40 grms. of hydrated sulphate of copper for a volume of 350 c.c. of bath. The deposit of peroxide of bismuth—of which the constitution Bi_2O_7 was given by a large number of experiments—is of a citron-yellow colour, and does not vary in weight when heated up to 180°.

The most highly oxidised oxide of bismuth yet known has the constitution Bi_2O_5.

We have not tried whether the constitution of the peroxides of nickel and of bismuth varies with the concentration of these metals. Besides, we have not been able to deposit quantities corresponding to more than 0·05 grm. of metal, which necessarily limits this examination.

Other Metals.

We have not examined the electrolytic peroxides of silver and manganese, which are the only electrolytic peroxides known, besides those we have just dealt with.

If other metals do not give electrolytic peroxides, this is apparently due to the fact that their peroxides are non-conductors of electricity.*

However, these peroxides can be obtained by depositing them with conducting peroxides. In this manner we succeeded in depositing with peroxide of lead, peroxides of antimony and of arsenic, and with manganese a peroxide of iron.† But what is the degree of oxidation of these peroxides we have not yet been able to determine. —*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 4.

THE USE OF A ROTATING CATHODE IN THE ELECTROLYTIC DETERMINATION OF THE METALS.‡

By F. A. GOOCH and H. E. MEDWAY.

THE rotating cathode has been applied usefully in the arts for the purpose of securing compact metallic deposits in electro-plating. In this case a soluble anode is employed, and the electromotive force of the current is generally low. So far as we are aware, however, no attempts have been made heretofore to apply the rotating cathode in analytical separations, in which it is the object to remove the metal completely from solution. In such processes the soluble anode is not used, and the comparatively high electromotive force necessary to overcome the resistances and to throw down the metal with rapidity liberates hydrogen from the water solution simultaneously with the metal, and the consequence is the production of a deposit lacking in compactness and adhesiveness. This interference on the part of the evolved hydrogen with the regularity of deposition appears to be the chief reason why low intensity and low density of current must be used in the ordinary electrolytic processes of analysis. We have made some experiments, therefore, to see whether it is not possible to so far avoid the interfering action of hydrogen by the use of the revolving cathode, as to secure with high currents and in a short time deposits sufficiently adherent and homogeneous for analytical purposes. The results, as will appear, are successful.

For a cathode we have used an ordinary 20 c.m.³ platinum crucible rotating at a speed of from 600 to 800 revolutions a minute. The crucible is driven by a small, inexpensive electric motor fastened so that its shaft is vertical. Upon this shaft the crucible is fixed by pressing it over a rubber stopper bored centrally and fitted tightly on the end of the shaft (Fig., A). To secure electrical connection between crucible and shaft, a narrow strip of sheet platinum is soldered to the shaft and then bent upward along the sides of the stopper, thus putting the shaft in contact with the inside of the crucible when the last is pressed over the stopper. The shaft is made in two parts as a matter of convenience in removing the crucible, and is joined, with care to make a good contact between the two pieces of shafting, by a rubber connector of sufficient thickness to prevent the crucible from wobbling when rotated.

The solution to be electrolysed is placed in a beaker upon a small adjustable stand, so that the crucible may be dipped into the liquid to any desired depth. A platinum plate is employed as an anode, and this is connected to the positive pole of a series of four storage batteries, while the negative pole of this series is connected to the bearing in which the shaft rotates, thus allowing the current to

* We omitted to try whether there was any nickel left in the bath at the end of this time. If there was any, the peroxide deposited corresponded to a degree of oxidation higher than NiO_4.

* In this case the system of electrodes used was that of Luckow (*Comptes Rendus*, vol. cxxiii, p. 23); the cone which served as the anode became, through prolonged usage and repeated calcinations, of a roughness which was preferable to that of recently platinised platinum.

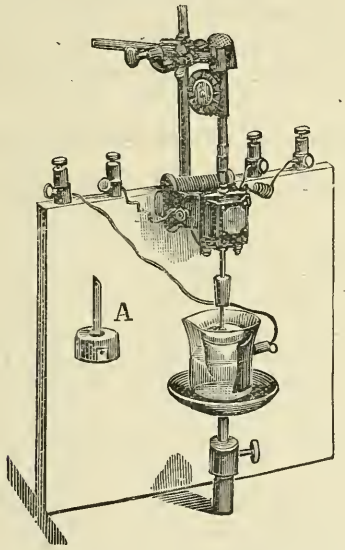
† The carrying down of iron with peroxide of manganese has been observed already by Neumann ("Analytische Elektrolyse," p. 194).

‡ Contributions from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, xv., p. 320.

go from the platinum plate through the solution to the crucible, up the shaft of the motor and back to the batteries.

The power to run the motor is taken from the incandescent light circuit of the street.

The first attempts were made with the deposition of copper from a solution of the sulphate, and the procedure was as follows:—The solution, 50 c.m.³ in volume, was placed in a 150 c.m.³ beaker and acidulated to give better conductivity. The stand carrying the beaker was raised until the liquid covered about two-thirds of the crucible adjusted to the shaft, thus giving a cathode surface of about 30 c.m.³. The anode was introduced and the motor started. The wires from the storage batteries were connected, and the current allowed to pass through the solution. The duration of the electrolysis was varied according to the strength of current used, but in each case, after the deposit was nearly complete, the current from the batteries was shut off, the motor stopped, and the sides of the beaker, the platinum anode, and the crucible were carefully washed with a fine jet of water, the motor was again started, and the current allowed to pass for the remaining time.



When the deposit was complete the crucible was removed and washed, first with water, then with alcohol, and finally was dried by passing it over a flame.

Sulphuric acid (6 or 7 drops of the dilute acid, 1 : 4) was generally used to acidulate the solution, since it was found that the copper was deposited in a shorter time with sulphuric than with nitric acid present. A few experiments were made in which small amounts of nitric acid were used to show that the copper could also be deposited completely in presence of this acid.

Table A shows the results of a series of experiments made as described above in solutions acidulated with sulphuric acid. The standard of the solution of copper sulphate was fixed by the usual slow method of electrolytic analysis.

That the copper can be completely deposited, though more slowly, from a solution acidulated with nitric acid, is shown in Tables B and C. In the experiments of Table B the solution contained 6 drops of dilute (1 : 4) nitric acid, and in those of Table C 9 drops.

The rapid deposition of silver was next tried. To a 50 c.m.³ solution of $AgNO_3$ was added enough potassium cyanide to dissolve the AgCN first formed. Three c.m.³ of dilute sulphuric acid were run in, and enough ammonia to make the solution strongly alkaline. The method of manipulation was exactly the same as in the case of copper.

Table A.

	Copper taken. Grm.	Copper found. Grm.	Error. Grm.	Current. Ampères.	$N.D._{100}$.	Time. Minutes.
1.	0·0651	0·0652	+0·0001	0·8	2·7	25
2.	0·0651	0·0652	+0·0001	0·8	2·7	15
3.	0·0651	0·0651	0·0000	1	3·3	10
4.	0·0651	0·0649	−0·0002	1	3·3	10
5.	0·0651	0·0648	−0·0003	1	3·3	10
6.	0·1272	0·1272	0·0000	2·5	8·3	15
7.	0·1272	0·1271	−0·0001	2·5	8·3	15
8.	0·1272	0·1271	−0·0001	2·5	8·3	15
9.	0·1272	0·1270	−0·0002	3	10	13
10.	0·1272	0·1268	−0·0004	3	10	12
11.	0·2548	0·2548	0·0000	3	10	20
12.	0·2548	0·2548	0·0000	4	13·3	20
13.	0·2548	0·2550	+0·0002	4	13·3	20
14.	0·2548	0·2546	−0·0002	4	13·3	15
15.	0·2548	0·2545	−0·0003	4	13·3	15

Table B.

Copper taken. Grm.	Copper found. Grm.	Error. Grm.	Current. Ampères.	$N.D._{100}$.	Time. Minutes.
0·0651	0·0648	−0·0003	1	3·3	35
0·0651	0·0652	+0·0001	0·8	2·7	30
0·0651	0·0650	−0·0001	0·8	2·7	25
0·0651	0·0649	−0·0002	1	3·3	25
0·0651	0·0650	−0·0001	0·8	2·7	25

Table C.

Copper taken. Grm.	Copper found. Grm.	Error. Grm.	Current. Ampères.	$N.D_{100}$	Time. Minutes.
0·0651	0·0652	+0·0001	1	3·3	35
0·0651	0·0648	−0·0003	1	3·3	30
0·0651	0·0650	−0·0001	1·5	5	25
0·0651	0·0650	−0·0001	1·5	5	25
0·0651	0·0647	−0·0004	1·8	6	20

Table D records the determinations made with a solution of silver nitrate standardised as the chloride.

Table D.

	Silver taken. Grm.	Silver found. Grm.	Error. Grm.	Current. Ampères.	$N.D._{100}$.	Time. Minutes.
1.	0·0968	0·0966	−0·0002	1·8	6	15
2.	0·0968	0·0967	−0·0001	1·9	6·3	15
3.	0·0968	0·0965	−0·0003	1·8	6	15
4.	0·0968	0·0969	+0·0001	2	6·7	10
5.	0·0968	0·0965	−0·0003	3	10	8
6.	0·1898	0·1901	+0·0003	2·5	8·3	10
7.	0·1898	0·1898	±0·0000	2·5	8·3	10
8.	0·1898	0·1900	+0·0002	3·	10	10
9.	0·1898	0·1893	−0·0005	2·5	8·3	10

The rapid deposition of nickel was equally successful. Nickel-ammonium sulphate was dissolved in 25 c.m.³ of water and 20 c.m.³ of strong ammonia were added. In this liquid about a grm. of ammonium sulphate was dissolved, and the solution was treated in the same manner as in the preceding experiments upon copper and silver. It should be especially noted, however, that the solution must be kept within the limits of volume indicated above, as further dilution lengthens the time necessary for complete deposition.

From the results in Table E it is plain that nickel, like copper and silver, may be deposited with rapidity and completeness.

The metallic deposits of these metals obtained by means of the revolving cathode are sufficiently coherent and compact to permit accurate manipulation and weighing, even when the current density on the cathode is very con-

siderable and variable within wide limits. Other metals have been found to behave similarly, and the results of further experimentation will be described later.

TABLE E.

	Nickel taken. Grm.	Nickel found. Grm.	Error. Grm.	Current. Ampères.	$N.D._{100}$.	Time. Minutes.
1.	0·0954	0·0954	0·0000	1·5	5	30
2.	0·0954	0·0953	−0·0001	3	10	25
3.	0·0954	0·0956	+0·0002	3	10	25
4.	0·0954	0·0953	−0·0001	3·5	11·7	20
5.	0·0954	0·0955	+0·0001	3·5	11·7	20
6.	0·1738	0·1736	−0·0002	3·5	11·7	25
7.	0·1738	0·1740	+0·0002	3·5	11·7	25
8.	0·1738	0·1740	+0·0002	4	13·3	25
9.	0·1738	0·1737	−0·0001	4	13·3	25
10.	0·1738	0·1738	0·0000	4	13·3	25

The advantages of this rotating cathode in analytical operation are obvious; the process as described is rapid, exact, and very simple. The apparatus required, moreover, is inexpensive, and, if it is desired to make many determinations simultaneously, a single motor may be made to drive a running belt over any reasonable number of rotating shafts.

NOTICES OF BOOKS.

Practical Chemistry; a Laboratory Course for Secondary Day Schools and Evening Classes. By WALTER HARRIS, M.A., Ph.D. In Three Volumes. London: Whittaker and Co. 1903. Pp. 410.

A HANDBOOK such as this will be useful alike to the teacher and the student, to the former by relieving him to some extent of a wearying number of questions, and to the latter by teaching him to help himself. The book is published in three separate volumes, which are devoted to:—(1) Measurement, (2) Exercises and Problems, and (3) Qualitative and Quantitative Analysis.

Accurate measurement is one of, if not the most important operations in chemistry, and the author has wisely put it in the first place, as students cannot be taught too soon the necessity for correct weighing and measuring. Density, specific gravity, volumetric measurements, &c., all come under this heading, and are dealt with in the first volume. Volume II. is more theoretical in its tone, and deals with the properties of the elements in regard to their mixing and combining with other elements, and the various phenomena which occur when chemical reactions take place.

Volume III., on Qualitative and Quantitative Analysis, takes the student through the routine work of detecting and recognising the various elements and salts, either alone or in mixtures, by means of their reactions and behaviour with reagents.

A careful student should obtain a very good elementary knowledge of chemistry by the help of this book.

Chemical Novelties for 1903. ("Les Nouveautés Chimiques pour 1903"). By CAMILLE POULENC, Dr. es Sc. With 186 Figures in the Text. Paris: J. B. Baillière et fils. 1903. Pp. 326.

THIS book will be very useful to chemists, as the author has dealt with all the latest laboratory apparatus and new methods of research, as applied to science and the arts, in a methodical manner.

In the first chapter we find full descriptions of new physical apparatus as applied to chemistry, such as apparatus for the determination of densities, of high temperatures, fusing-points, &c.

Chapter II. comprises new apparatus for chemical manipulation, gas-burners, ovens, temperature regulators, extraction apparatus, and new methods of producing gases, &c.

Chapter III. deals with chemical apparatus in the use of which electricity is employed, such as regulators, transformers, interruptors, voltmeters, &c. The introduction of electricity, by the electrolytic phenomena it brings about, as well as by its thermal action, has carried chemistry along a new and prolific path, and at the same time has been the cause of the introduction of new methods into laboratories; it has given us fresh means of investigation of a high value. By its use we have now at our command the means of obtaining the highest temperatures with the greatest rapidity, combined with exact and simple regulation.

Chapter IV. is devoted to chemical analysis in general, with special sections for gas analysis, metallurgical assaying, technical analysis, and special apparatus for the examination of foods and drugs.

Chapter V. and last deals with the new and interesting apparatus introduced for the study and application of bacteriology. Among these we may mention an ingenious method for taking samples of water for chemical and bacteriological examination at one and the same time, while preventing the possibility of any external contamination of the sample.

The book contains a complete table of contents and a good index.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 19, May 11, 1903.

Researches on the Law of Electromotive Forces developed by Reciprocal Actions of Saline Solutions.—M. Berthelot.—The author examines the relation existing between the electromotive force developed by the action of an acid on a base (E) and the forces developed by the action of the corresponding salt, firstly, on the acid (E_1), and then on the base (E_2). He establishes, by exact measurements on electrodes incapable of polarisation, the law that $E = E_1 + E_2$. The experiments were all performed with dilute solutions containing the equivalent weight of each body dissolved in the same volume of water. Six acids and two bases were used in the research.

Electrolysis of Alkaline Sulphides.—André Brochet and Georges Ranson.—When electrolysing a concentrated solution of sulphide, the authors find that, at a given moment, the needle of the voltmeter and that of the ammeter oscillate in a regular manner. The amplitude of the oscillations is greater according as the density of the current is increased; this phenomenon is due to the deposition and to the successive solution of a thin layer of sulphur on the anode. In all the series of experiments, with or without a diaphragm, potassium sulphide behaves exactly as sodium sulphide. In fact, the electrolysis of an alkaline sulphide gives, according to the conditions of concentration, either sulphur or compounds due to its oxidation, the final one being sulphuric acid.

Benzene-azo-orthobenzylic Alcohol and its Transformation into Phenyl-indazol and Azodiphenylmethane.—P. Freundler.—The author obtains benzene-orthoazobenzylic alcohol by the condensation of nitrobenzene with ortho-aminobenzylic alcohol in presence of alcohol and acetic acid. This substance possesses the singular property of dehydrating with the greatest ease under various influences. When heated to about 80° with a 50 per

cent sulphuric acid solution, it is quantitatively transformed into phenyl indazol. This phenyl indazol is also produced when benzene-azo-benzylic alcohol is heated above 130° *in vacuo* or at ordinary pressure, but in this latter case it is accompanied by a certain quantity of an isomeric compound which can only be azodiphenylmethane.

Organo-metallic Derivatives of Di-halogen Aromatic Hydrocarbons. Action of Iodine.—F. Bodroux.—Di-halogen aromatic hydrocarbons form poly-substituted bodies capable of forming compounds with magnesium in presence of ether. The author thus transforms—Dibromobenzene-1.4 into parabromoiodobenzene, dibromobenzene-1.3 into metabromoiodobenzene, bromochlorobenzene-1.4 into parachloroiodobenzene, and dibromonaphthalene-1.4 into bromoiodonaphthalene.

Methylation of Ethylglutaconate.—E. E. Blaise.—The author continues a previous research on the methylation of ethylglutaconate at 0°. He now conducts his researches at higher temperatures, and succeeds in introducing a third methyl group into the molecule of glutaconic acid.

Migration of the Methyl Group in the Molecule of Camphor.—G. Blanc and M. Desfontaines.—This paper describes a continuation of a former research on the structural change in the camphor molecule.

Successive Action of Acids and Soluble Ferments on Polysaccharides of High Molecular Weight.—Em. Bourquelot and H. Hérissey.—The authors establish the fact that the polysaccharides which are more condensed than gentianose can only be hydrolysed by the action of certain ferments.

Diastasic Decomposition of Salol.—E. Pozzi-Escot.—The author finds that the saponifying ferments of vegetable grains, which are very active towards the ether functions of the acyclic fatty acids, have scarcely any action towards the phenolic ether functions. In other cases he utilises free phenol as an antiseptic agent without sensibly destroying the saponifying action of vegetable lipases. There can, however, from all the experiments performed, be no question as to the destructive influence of the phenol resulting from the saponification of salol.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 8th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Sir Walter J. Sendall, G.C.M.G., was elected a Member.

Change of Address.—Mr. Bertram Blount, consequent on the death of his partner, has removed to 76-78, York Street, Westminster, where he will continue in practice under his own name.

The Faraday Society.—The Council of this Society begs to draw the attention of members to the following arrangements that have been made:—(1) The Proceedings of the Society will be published in *The Electro-Chemist and Metallurgist*," which will be published monthly, free to members. (2) All papers presented to the Society will be printed and circulated among the members before being read, and, as a rule, they will be read in abstract only. Members and others unable to be present will be asked to send their contributions to the discussion in writing, and their remarks will be read out to the meeting. By this means it is hoped greatly to increase the value of the discussions, and to give absent members an opportunity of expressing their views.

The Dinitration of Hydrazine.—M. Betti.—When we wish to effect the dinitration of hydrazine, we always obtain the azoimide through the action of the H_2N- on the oxide of azonium which is formed first, on the other NH_2 : $H_2N-N=NOH=H_2O+N_3H$. However, we can obtain a chain of 4N by reacting with hydrazine on nitroso-acetylacetic ether. For this purpose we use a solution of sulphate of hydrazine, which is made to react on a solution of 2 molecules of nitroso-ether. After seven hours' contact we obtain a product of condensation in the form of canary-yellow needles, insoluble in water, but soluble in alcohol, from which it crystallises in flakes or in cubes, fusible at 197°. The most probable formula is—

$$\begin{matrix} CH_3-CO \\ C_2H_5-O_2C \end{matrix}\!\!>\!CH-N=N-N=N-CH\!<\!\begin{matrix} COCH_3 \\ CO_2C_2H_5 \end{matrix}.$$

The Na_2 salt is crystalline, and forms a citron-yellow solution in water. It deflagrates with heat, and precipitates the salts of the heavy metals.—*Gazz. Chim. Ital.*, vol. xxxii., [II.], p. 146.

The Composition of Rapidly Setting Cements.—O. Rebuffat.—Commercial quick setting cements are all natural products. If we try to make artificial cements we observe that the mixture of kaolin or clay, with lime or crystalline carbonate of lime, does not give a coherent cement; on the other hand, we obtain a cement which sets very rapidly if we use amorphous $CaCO_3$, prepared by precipitating $CaCl_2$ by Am_2CO_3 in the cold. Further, it is very remarkable that lime prepared from crystalline $CaCO_3$ becomes hydrated very rapidly, while that prepared from amorphous $CaCO_3$ is quite porcelainic, and does not react with water. A mixture of $2SiO_2$, $2Al_2O_3$, and $5CaO$, burnt, and then submitted to the action of water, does not give a very coherent cement, although its formula corresponds to that of a good one. The temperature of baking a rapid setting cement should be from 700 to 800°; at 1100° to 1300° it becomes much slower, and then loses its property of setting. The best proportion to use is $2(SiO_2,Al_2O_3)6CaO$. It is not necessary for a rapid setting cement to contain free SiO_2. *The Chemical Properties of Artificial Kaolin Cements.*—For the burning to have taken place between 800° and 1200° the amount of CaO soluble in syrup should offer but slight variations. After hydration the amount of lime soluble in syrup is different to that of the anhydrous product; thus water plays another part besides that of hydration. By burning a mixture of $2SiO_2,2CaO+Al_2O_2,2CaO$ at 800°, we obtain a product that swells up considerably in water without setting; by baking for eight days, it gives, on the other hand, a cement setting very rapidly.—*Gazz. Chim. Ital.*, vol. xxxii., [II.], p. 254.

The Periodates of Lead and Copper.—F. Giolitti.—$Pb.HIO_5$.—A solution of acetate of lead acidulated with acetic acid, gives a white precipitate with dipotassic iodate, K_2HIO_5. When dried it turns slightly yellow, and becomes crystalline. At 140° it loses water, and changes to $Pb_2I_2O_9$, an orange-yellow powder insoluble in water. In two experiments, and without the author having been able to determine the difference of the conditions, a yellow precipitate of $Pb_3I_2O_{10}\,2H_2O$ was obtained instead of $PbHIO_5$. On the other hand, freshly precipitated $PbHIO_5$ gives, on boiling with acetate of lead, an orange-yellow powder of $Pb_3I_2O_{10}$. $PbHIO_5.H_2O$.—This salt is obtained by precipitating acetate of lead by an aqueous solution of periodic acid; it is a white powder, losing H_2O at 110°. Pb_2HIO_6.—$PbHIO_5$ submitted to prolonged boiling in water, gives this salt in the form of a brown crystalline powder. $Pb_3I_2O_{10}H_2O$.—A solution of $PbHIO_5$ in nitric acid is treated with the freshly precipitated hydrated lead; it is a white crystalline powder. *Periodates of Copper.*—$CuHIO_6$ is a green powder obtained by precipitating a solution of acetate of copper by K_2HIO_5; it loses water at 120°, and forms the salt $Cu_4I_2O_{11}$, which is a brown powder. $Cu(IO_4)_2$.—A sky-blue precipitate obtained by boiling acetate of copper with periodic acid. $Cu_5I_2O_{12}.7H_2O$ is a dark green precipitate obtained by boiling the precipitate formed by K_2HIO_5 and a large excess of acetate of copper, in ammonia. The hydrate, $Cu_5I_2O_{12}.3H_2O$, is obtained in the form of a yellowish

green powder by dissolving Cu_2HIO_6 in nitric acid, then adding hydrated oxide of copper, and boiling the solution. —*Gazz. Chim. Ital.*, vol. xxxii., [II.], p. 340.

Catalytic Oxidation of the Alcohols (the Case of the Platinum Spiral).—A. Trillat.—In summing up the most interesting points in the catalytic action of platinum, and of porous bodies in general, on the alcohols, the author observes that the primary alcohols gave the corresponding aldehydes; the secondary alcohols, a ketone; while the tertiary alcohols gave principally the ketone immediately below formic aldehyde. Contrary to the opinion of several chemists, water is not an obstacle to the chemical phenomena due to contact action. The temperature at which oxidation by contact with the platinum spiral commences to take place is lower than 200°. In most of the cases examined, the heat given off by the oxidation of the alcohols, or by their molecular disaggregation, is capable of maintaining the platinum spiral in an incandescent state. By oxidation with platinum black, the action is less limited, and approaches that of chemical agents. In such cases, acids and ethers were obtained frequently, instead of aldehydes. The mechanism of oxidation observed is as follows:—In the case of a moderate oxidation the action is limited strictly to the formation of the corresponding aldehyde with a more or less considerable proportion of acetal; at least this is so for the first terms of the alcohols of the fatty series. A more energetic oxidation (white heat with excess of oxygen) has the effect of transforming the aldehyde into the corresponding acid, which is itself easily dissociated. As secondary products, the formation of ether resulting from the combination of the acid with the alcohol has been observed.—*Bull. Soc. Chim. de Paris*, xxix., No. 1.

MEETINGS FOR THE WEEK.

WEDNESDAY, 17th.—Microscopical, 8. "On the Theory of Optical Images, with special reference to the Microscope," by the Rt. Hon. Lord Rayleigh, F.R.S. "On a Method of making Visible Ultra-microscopic Particles in Glass, and the Application of the Method to Bacteria," by Dr. H. Siedentopf. "On the Lag in Microscopic Vision," by E. M. Nelson.

— Chemical, 5. "The Estimation of Arsenic in Fuel" and "The Electrolytic Estimation of Minute Quantities of Arsenic, more especially in Brewing Materials," by T. E. Thorpe. "Crystallised Ammonium Sulphate, and the Position of Ammonium in the Alkali Series," by A. E. H. Tutton. "Action of Hydrogen on Sodium," by A. Holt, jun. "The Action of Halogens on Compounds containing the Carbonyl Group" and "Reactions involving the Addition of Hydrogen Cyanide to Carbon Compounds," by A. Lapworth. "The Acetoacetic Ester Synthesis," by A. C. O. Hann and A. Lapworth. "Rimu Resin" and "Note on the Karaka Fruit," by T. H. Easterfield and B. C. Aston.

FRIDAY, 19th.—Royal Institution, 9. "Radium" (in French), by Prof. Pierre Curie.

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Re Pirie *v.* The Company and Others.—The Electro-Chemical Co. (1900), Ltd., 1901, E. 85.—By orders of Mr. Justice Farwell.

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THE CHEMICAL NEWS.

VOL. LXXXVII., No. 2273.

THE DETERMINATION OF CARBON IN STEEL BY DIRECT COMBUSTION IN OXYGEN.

By LAWRENCE DUFTY.

THE simplest method that has been suggested for the determination of carbon in steel is undoubtedly the direct combustion of the sample in oxygen. But although this method was used for pig-iron as far back as 1862 by Mulder (CHEMICAL NEWS, vol. v., p. 5), and later for steel by Herman with good results (CHEMICAL NEWS, vol., xl., p. 263), the opinion generally prevalent appears to have been that the process was uncertain and the results low. Within the last few years, however, Rozyetti (*Journ. Soc. Chem. Ind.*, 1899) and Blount (*Analyst*, 1902) have shown that the method is reliable if necessary conditions are adhered to.

As a result, the process—more or less modified—seems to be gradually coming into favour, and not without good reason, for if the essential condition be strictly observed, viz., that the drillings used be sufficiently thin, the process gives perfectly accurate results, and a carbon determination can be made in the remarkably short time of forty minutes or less from time of receipt of sample. Thin curly drillings may be simply placed in a boat and burnt in oxygen without any reagent. As a general rule, however, especially if the drillings are very small or inclined to be powdery, it is necessary to mix with some material which will separate the particles and, if possible, assist in the oxidation of the sample without fusing to a liquid mass, as is the case when using the oxides of lead or bismuth, as recommended by Brearley (CHEMICAL NEWS, vol. lxxxiv., p. 23), and Leffler (CHEMICAL NEWS, vol. lxxxv., p. 121). Rozyetti used Al_2O_3, Rhead and Sexton ("Assaying and Metallurgical Analysis") suggest MgO, whilst Brearley and Ibbotson ("Analysis of Steel Works Materials") find ZnO satisfactory for certain alloys; other oxides suggested are SiO_2, CaO, SnO_2 Mn_3O_4, &c.

In order to ascertain if any one oxide had an advantage over another, a series of combustions were done with steels mixed with Al_2O_3, ZnO, MgO, CaO, $S O_2$, Mn_3O_4 and SnO_2 respectively. All gave almost identical results, and all remained "dry" (and mostly uncombined), except CaO, which forms with the oxide of iron a slag just fusible at the usual temperature of the furnace used.

As the advantage, if any, seemed to be with MgO, Al_2O_3, and CaO, the first of these was chosen, and the direct process thoroughly tested, using this oxide throughout. The method adopted was as follows:—

2·727 grms. of drillings (not exceeding 0·5 m.m. in thickness for hard, and 0·25 m.m. for mild steels), or 1·3636 grms. of pig-iron (grey pig is powdered until it all passes through a sieve 40 meshes to the inch), are mixed with ½ grm. of freshly ignited MgO by shaking in a weighing bottle, and then transferring to a boat containing a layer of MgO—a further portion of the oxide being spread over the top to cover any drillings exposed. (If the magnesia gives any "blank," a definite quantity must always be used and the blank deducted). Having placed the boat in the red-hot tube, the aspirator is set working, and at the end of a few minutes—sufficient time being given for the boat to attain a red heat—the oxygen is turned on, and, as soon as the steel begins to burn, is allowed to enter at a decidedly rapid rate. At this stage very little gas passes through the KOH absorption bulb, practically all the oxygen combining with the steel. When the gas bubbles through the absorption bulb at about the same rate as that at which it enters the furnace, the oxygen is turned off (the combustion of the sample being complete), and about a litre of air is passed through, the absorption bulb being then detached and weighed. The increase in weight, minus the blank, multiplied by 10 or 20, according to the weight taken, converts the CO_2 to carbon per cent.

The results obtained from a series of standard steels by the above method are compared in the following table with those obtained by solution in copper-ammonium chloride and combustion of the dried carbonaceous residue.

	Sample.	Carbon, per cent. Ordinary solution method.	Direct with MgO and O.
1.	Steel	0·22	0·22, 0·23
2.	,, ...	0·29	0·30, 0·30
3.	,, ...	0·48	0·48, 0·49
4.	,, ...	0·62	0·63, 0·62
5.	,, ...	0·87	0·87, 0·88
6.	,, ...	1·07	1·09, 1·08
7.	,, ...	1·20	1·22, 1·22
8.	,, ...	1·45	1·47, 1·47
9	,, ...	2·29	2·32, 2·29
10.	,, ...	2·47	2·50, 2·53
11.	White pig.. ..	3·57	3·60
12.	,, ...	3·82	3·84
13.	Grey pig	4·04	4·05
14.	,, ...	4·12	4·12
15.	,, ...	4·36	4·32

In dealing with special steels and alloys, the solution method is always more or less troublesome when tungsten or molybdenum is present in any quantity, and the results are generally unsatisfactory, often decidedly so. For such steels a direct method is really the only way by which the full carbon contents can be ascertained.

By the process given above, special steels and alloys, when in the form of drillings, give up the whole of their carbon almost as readily as ordinary steels. It is essential, however, when chromium is present to any appreciable extent, that the drillings do not exceed ¼ m m. in thickness. (With a little experience this can be judged by the eye). In the following table it will be noticed how consistently low are the results obtained by the ordinary combustion process, when compared with the direct, for samples containing large amounts of chromium and tungsten or molybdenum.

	Special contents, per cent.	Carbon, per cent. Ordinary solution method.	Direct, with MgO and O.
16.	Ni .. 3·8	0·34	0·36
17.	Ni .. 23·0	0·79	0·82
18.	Cr .. 1·0	0·88	0·90
19.	Cr .. 4·7 Si .. 2·5	1·76	1·79
20	Mo .. 4·1	0·77	0·88
21.	Mo .. 5·1 Cr .. 4·0	0·64	0·84
22.	W .. 2·8	1·24	1·27
23.	W .. 4·8	0·55	0·59
24.	W .. 9·1 Cr .. 5·1	0·44	0·51
25.	W .. 11·0 Cr .. 6·5	0·36	0·42
26.	W .. 20·2 Cr .. 4·7	0·59	0·67
27.	W .. 21·5 Cr .. 7·0	0·90	Direct, with Pb_3O_4. 0·92
28.	W .. 32·0 Cr .. 10·0	1·60	1·61

In most of the foregoing combustions, and in many others, the drillings used were as usually supplied to the laboratory—no special drilling being found to be necessary, except in the case of mild and a few special steels.

Alloys which will not drill after careful annealing, if

powdered and ground to a fine state of division in the agate mortar and then well shaken with MgO or CaO, will, in the majority of cases, burn completely in oxygen. Some ferro-chromes, even, will oxidise if thoroughly "floured" in the mortar and ignited for a sufficient length of time.*

A few results of some manganese alloys, which generally have their carbon percentage determined by the solution method, are given as illustrating the higher, and no doubt correct, results obtained by the direct magnesia process.

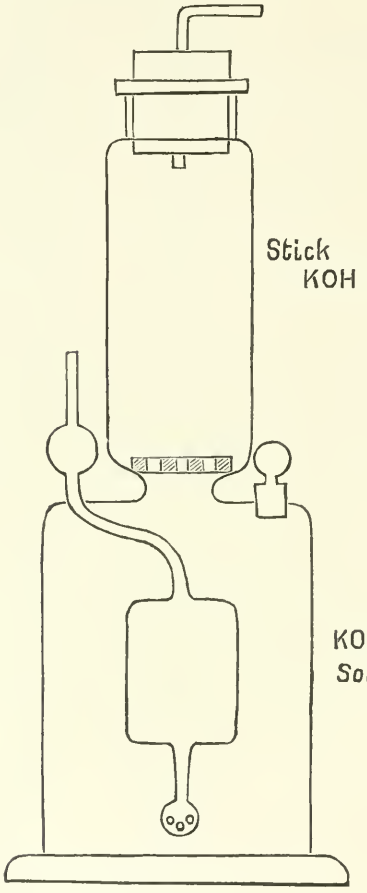


FIG. 1.

	Carbon, per cent.	
	Ordinary solution method.	Direct, with MgO and O.
29. Ferro-manganese (80 per cent)	6·69	6·88
30. Do.	6·55	6·70
31. Do.	6·88	7·05
32. Spiegel (20 per cent) ..	4·69	4·87
33. " " ..	5·96	6·06
34. Silico-spiegel	1·89 / 1·90 Oxygen alone.	2·14 / 2·16

Although silico spiegels, as a rule, burn completely in oxygen without any reagent, the results of the sample quoted above shows the advisability of always using an oxide with these alloys.

* For these very refractory alloys, however, the use of Bi_2O_3 or Pb_3O_4, as recommended by Brearley (CHEMICAL NEWS, vol. lxxxiv., p. 23), is to be preferred as being quicker and more certain of giving the full carbon contents.

From what has been stated it will be apparent that the direct combustion process is not only an alternative to the usual solution method, strongly appealing to the steel-works chemist on account of its reliability, simplicity, and speed, but, as shown, such a direct method is absolutely essential in the case of most special steels and some alloys, if an accurate determination of the carbon is to be made.

A few notes on the process, and details of the apparatus used, may be of service.

When a combustion is finished, the boat is withdrawn, its contents turned out by means of a piece of wire or the tang of an old file, and then re-charged with the next sample. The oxidised drillings should always frit together in the form of a long cake, which is very easily extracted owing to the boat being protected by the unfused magnesia.

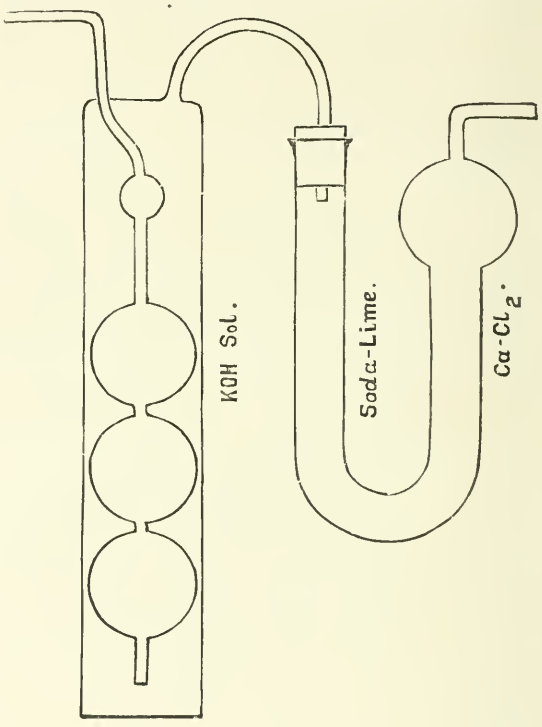


FIG. 2.

If the steel should not have been completely burnt, the drillings will be detached from each other—no fritting whatever having taken place. In this case either thinner drillings are required, or more heat should be applied.

Both MgO and CaO require igniting at a high temperature in the muffle to completely drive off CO_2, and, in the case of lime that has been prepared from marble, it is advisable to do a blank of each batch after ignition. As these oxides, however, absorb CO_2 from the air, their use has lately been discarded in favour of Al_2O_3, which, after ignition in the muffle, gives no blank, nor does it absorb CO_2; on this account it is preferable to either of the other two, and is now regularly used by the author as a standard reagent.

The furnace used is of the Bunsen type, with Finkener's burners, but the firebrick clays are replaced by asbestos arches with an extra arch over the boat as illustrated by Leffler (CHEMICAL NEWS, vol. lxxxv., p. 121). This arrangement ensures a sufficiently high temperature—no blast whatever being required. The combustion tube (porcelain 26" × 1⅛") is covered with asbestos cloth or mill-board. It is packed as usual with a few inches of copper oxide, and the cooler exit portion with granular

fused lead chromate to absorb sulphur compounds—the CuO and $PbCrO_4$ being separated by a large asbestos plug.

The gas purifying apparatus consists of a combined wash-bottle and tower as illustrated in Fig. 1.* The lower portion contains strong KOH solution through which the gas bubbles, and then passes through the top portion, which is filled with stick KOH supported by a perforated porcelain plate. The oxygen (from cylinder) and air have each their separate washing apparatus. Fig. 2 shows the absorption apparatus used, which consists of a modified Arnold's KOH bulb to which is attached a U-tube by means of a good fitting rubber cork. The addition of a third bulb to Arnold's tube increases its capacity to about 25 c.c., and as there is a corresponding increase of potash surface exposed to the gases passing through, it is made thoroughly efficient for very rapid working. The attached U-tube is two-thirds filled with dry calcium chloride, and one-third with soda-lime. The latter reagent should be replaced as soon as it becomes hydrated; in this manner the $CaCl_2$ will remain dry, and act as a safety-guard for a considerable period. The combined apparatus is suspended on the balance (Bunge's) by the bent exit tube of the KOH bulb. A similar bulb and tube containing respectively pure H_2SO_4 and $CaCl_2$ are placed in front of the absorption bulb to dry the gases. The apparatus illustrated may be obtained from J. J. Griffin and Sons, London.

The Laboratory,
Continental Steel Works, Sheffield.

NEW ETCHING FLUID FOR MICRO-METALLURGY.

By WM. RAMSAY, A.I.C.

Among the various etching solutions used in demonstrating the microstructure of alloys, and especially those of copper, ammonia finds a prominent place. The reaction depends largely on the absorption of atmospheric oxygen, and if the specimen is deeply immersed the etching proceeds very slowly; on the other hand, if it be near the surface the etching is relatively quicker, but apt to be irregular; so that successful etching, in many cases, can only be accomplished with great loss of time. Secondary reactions may also occur, especially with the alloys of the Cu-Zn and Cu-Sn series, crystalline patches of metallic copper being deposited, also insoluble oxides and carbonates to such an extent as to entirely mask the original structure of the polished surface.

In order to obviate these defects the author sought to introduce the necessary free oxygen into the ammonia by means of hydrogen peroxide, and was gratified to find the addition all that could be desired. The reaction takes place energetically, and is complete in a few seconds to a few minutes according to the strength of the mixture and the amount of etching required.

My usual procedure is to immerse the specimen in more or less dilute ammonia and then to gradually introduce H_2O_2 by means of a pipette. Oxygen is at once evolved and the etching takes place rapidly, evenly, and without any of the after effects produced by long etching. The crystalline facets and edges of the constituents are more clearly defined and often beautifully differentiated in various tints and colours.

For many purposes I find this new reagent better than ammonia, nitric acid, ferric chloride, &c., and feel confident that it will prove of value in the hands of other workers.

Birkenhead Iron Works,
June 9, 1903.

* This design is now being slightly modified, in order to overcome difficulties of manufacture.

QUALITATIVE AND QUANTITATIVE ANALYSIS OF COBALT COMPOUNDS.

By H. COPAUX.

The examination of cobalt compounds has enabled me to make certain analytical observations, which I have collected together in this paper.

Metallic cobalt and its compounds, such as they are met with commercially, are never pure. They often contain sulphur, phosphorus, copper, aluminium and lime, and always iron and nickel. When we have to deal with traces of impurities in a large excess of cobalt, and wish to purify the latter for example, the general qualitative method is found to be insufficient, and it is necessary to have recourse to more sensitive methods.

Those which I am about to describe, based, however, on known principles, have enabled me to recover 1 m.grm. of foreign metal in 1 grm. of cobalt. Further, as the estimation and separation of the cobalt still offers some difficulties in its execution, I have set myself to remove these difficulties in the second part of this research.

Detection of Impurities.

The Heavy Metals.—Sulphuretted hydrogen suffices to detect the presence of traces of the heavy metals in a slightly acid solution.

Zinc and Manganese.—To the dilute hydrochloric solution, add freshly dissolved cyanide of potassium until complete limpidity is obtained. Make alkaline with soda, then add a few drops of sulphide of sodium. The sulphides of zinc and manganese are precipitated without carrying down any cobalt.

Iron.—To the dilute solution add sulphocyanide of ammonium and compare the colour of the mixture with that of the original solution.

Nickel.—Though we can detect the presence of 1 part of cobalt in 2000 parts of nickel, by means of Ilinski and von Knorre's nitroso-β-naphthol (*Berichte*, vol. xviii., p. 699), the inverse problem is much more delicate.

Detection of Nickel by means of Cyanides.—Among the classic methods the best is that of Liebig, based on the difference in stability of the double cyanides in the presence of alkalis. To the solution of the chlorides we add an excess of cyanide of potassium, then bromine and potash. The cobalticyanide of potassium remains unchanged in solution; the double cyanide of nickel is transformed into the brown hydrated sesquioxide, which is precipitated.

This hydrate has no characteristic appearance. From the qualitative point of view, this is the great drawback to the method, which is, however, sensitive to one-thousandth part.

Detection of Nickel by means of Carbonic Oxide.—Messrs. Mond, Langer, and Quincke, in their paper on carbonyl of nickel (*Chem. Soc.*, 1890, vol. lvii., p. 749) advise the application of carbonic oxide to the detection and elimination of nickel in cobalt.

My experiments do not confirm this; they show, in fact, that the reaction, which is very sensitive with pure nickel, becomes the less so as the proportion of cobalt increases.

The metals in synthetic mixtures are precipitated in the state of hydrates. After reduction by hydrogen at 375–380°, then cooling in this gas down to 55—60°, I passed a current of carbonic oxide. The two dry gases, freed from oxygen by means of a tube containing red-hot copper, then dried again, were passed over the material and finally found their way into a capillary glass tube heated to about 400°.

Results.

1 m.grm. of pure Ni, gave a beautiful metallic ring, 6 to 7 c.m. in length.

1 m.grm. of Ni, and 0·1 m.grm. Co, gave a greyish transparent ring 1 c.m. in length.

1 m.grm. of Ni, and 1 m.grm. Co, gave an insignificant grey stain.

The diffusion of the metals in an inert body, such as alumina, did not improve the results.

The nickel remained in the residue with the cobalt. I made sure of this by the following means.

Detection of Nickel by means of Ether saturated with Hydrochloric Acid Gas.—M. Pinerua proposed in 1897 (*Comptes Rendus*, 1897, vol. cxxiv., p. 862), to separate nickel from cobalt by the difference of solubility of the chlorides in ether saturated with hydrochloric acid gas. The cobalt forms a soluble hydrochlorate of the chloride; the nickel is precipitated in the form of anhydrous chloride, yellow, crystalline, and very characteristic.

I have nothing to add to M. Pinerua's remarks, except that it is very easy to detect 1 m.grm. of nickel in 1 grm. of cobalt, and that on this principle I have based a method for the purification of cobalt. Ether, saturated with hydrochloric acid gas, in my opinion, is the best reagent for detecting traces of nickel in cobalt.

Quantitative Analysis.

I will limit myself to the question of the estimation of cobalt in the presence of nickel. Among the numerous reagents proposed, I prefer two only; nitroso-β-naphthol and nitrite of potassium.*

Nitroso-β-naphthol.—This reagent, of which I have already mentioned the extreme sensitiveness, precipitates cobalt from its hydrochloric solutions in the state of insoluble cobaltinitrosonaphthol. The corresponding compound of nickel, of which also the constitution is different, is, on the other hand, soluble.

The process has not been generally used for two reasons, viz., the considerable volume of the cobaltic precipitate, and, above all, the difficulty of calcining this body without loss owing to its being slightly explosive.

In 1893, von Knorre (*Zeit. Angew. Ch.*, 1893, p. 261) made an ingenious proposal, viz., to heat the moist precipitate, enveloped in its filter-paper, very rapidly in a platinum crucible. Under these conditions the substance is burnt without fusing.

Further, he proposed to weigh the product of the calcination, such as it was, and to consider it as being the oxide Co_3O_4; this, however, is inadmissible. Rose and Rammelsberg, in fact, have shown long ago that the calcined oxide of cobalt is a mixture of a variable composition.

I made another modification in this method, which consists of re-dissolving the oxide in concentrated hydrochloric acid, evaporating to dryness, and electrolysing the chloride in the presence of oxalate of ammonia. The results are fairly satisfactory.

	Theory.	Found. I.	Found. II.
Co	0·188	0·1899	0·1901
Ni	0·200	—	—

Still, the method is by no means so good as the following one, either in exactitude or convenience.

Nitrite of Potassium.—The cobaltico-potassic nitrite or cobaltinitrite of potassium, used in analysis since the time of W. Fischer in 1847, is a mixture of several salts (Rosenheim and Koppel, *Zeit. Anorg. Ch.*, 1898, vol. xvii., p. 35). The most abundant has the formula $Co_2(NO_2)_{12}K_6.2H_2O$. Its constitution is analogous to that of the cobalticyanides and of the cobaltioxalates of which I have written recently (*Comptes Rendus*, vol. cxxxiv., p. 1214).

The technique of the nitrite method, such as it is described in text-books of analysis, is the result of a research published by Gauhe in 1866 (*Zeit. Anal. Ch.*, 1866, vol. v., p. 74). It takes two or three days to make an analysis, and the instructions given are by no means sufficiently explicit; it is sometimes impossible to obtain any definite results. The whole of this want of success is due to the nitrous acid, and a complete precipitation can be obtained in twelve hours at the outside by operating in the following manner:—

Reagents.—(1) Nitrite of potassium at 40 per cent, slightly acidulated with nitric acid; (2) the same solution diluted to one quarter (10 per cent of nitrite).

Precipitation.—The solution of chlorides or nitrates, free from the heavy metals, from iron and the alkaline earths, is concentrated up to from 1 to 5 per cent of cobalt, and placed in a conical flask. One c.c. of concentrated nitric acid is added, then 15 c.c. of nitrite at 40 per cent. Instantly, and with effervescence, an orange-yellow precipitate of cobaltinitrite is formed.

When the solution has become perfectly clear, it is filtered through a small filter, and the precipitate washed with 15 c.c. of nitrite at 40 per cent, which is added to the mother-liquors with 0·5 c.c. of nitric acid.

After twelve hours, add the second precipitate to the first, and wash the whole with solution No. 2.

A third precipitation is rarely of any use unless the liquors become cloudy during filtration.

Solution and Electrolysis.—Place the precipitate with its filter in the flask used for precipitation, dissolve in hot dilute sulphuric acid. The filtered solution being neutralised with solid carbonate of ammonia, we add 4 or 5 grms. of oxalate of ammonia,* then electrolyse with a current of about 1 ampère per square decimetre, and an electromotive force of 3 to 4 volts.

	Co.	Ni.	Co.	Ni.	Co.	Ni.
Theory ..	0·1880	0·200	0·0188	0·200	0·1880	0·020
Found ..	0·1878	—	0·0194	—	0 1874	—

We see that the accuracy of the results is quite independent of the relative proportions of the two bodies present.

Analysis of an Asbolane,—I have applied the preceding method to the analysis of an asbolane (Herrenschmidt, *Mon. Scient.*, 1892, p. 359). Asbolane is a mineral of cobalt, which occurs very abundantly in New Caledonia; it is a compound of binoxide of manganese with protoxides in very variable proportions, according to the locality. It does not contain either arsenic or heavy metals. The sample I examined contained Mn, Co (6·2 per cent, Ni, Fe, and Al, with traces of Ba, Ca, Li, K, and Na. The whole difficulty of the analysis rests in the preliminary separation of the iron and aluminium, without carrying down any cobalt or manganese.

If a complete analysis is desired, carbonate of baryta is the only separating reagent that can be relied upon absolutely. If we wish merely to know the proportion of cobalt present, we can do this more rapidly by making the iron alone insoluble by M. Nicolardot's excellent method (*Comptes Rendus*, 1901, vol. cxxxiii., p. 686). For the sake of brevity I will give only the principle of the operations.

Complete Analysis.

Iron and Alumina.—Double precipitation with carbonate of baryta in the cold, in the presence of hydrochlorate of ammonia.

Nickel and Cobalt.—Precipitation by sulphuretted hydrogen, in acetic solution, of the filtrate freed from barium. The sulphides being re-dissolved in bromised hydrochloric acid, separate the cobalt by means of nitrite. On another sample, estimate the nickel by Liebig's cyanide process.

Manganese.—Estimation in the state of sulphide in the solution freed from iron, aluminium, nickel, and cobalt.

Abridged Analysis.—Heat the chlorides to 125° for several hours, and take up with sulphate of ammonia. Filter off the basic sulphite of iron, precipitate the filtrate

* Pinerua's method has given M. Carnot good results in the analysis of steels poor in nickel, but it is more applicable to the estimation of this latter metal than to that of cobalt. The same may be said of the cyanide methods.

* Oxalate of potash, recommended by Classen, carries a surcharge of 1 to 2 m grms. on the metallic deposit.

with sulphuretted hydrogen in aceti solution, and complete as before.

Results.

MnO	38·2
CoO	7·9
NiO	3·6
Fe_2O_3	3·5
Al_2O_3	18·8
Alkalis and alkaline earths	1·2
Active O	9·4
Total H_2O	15·8
SiO_2 and chromite	0·5
	98·9

Conclusions.—The question, so often discussed, of the analytical relations between nickel and cobalt, can be summed up as follows:—Carbonic oxide is a sensitive reagent for pure nickel, but it loses all its advantages when the nickel is allied with an excess of cobalt.

Qualitatively, ether saturated with hydrochloric acid gas is the reagent most likely to detect traces of nickel in cobalt.

Quantitatively, nitrite of potassium, used as I have described, remains the best reagent for the direct separation of cobalt, in a mixture containing cobalt and nickel.—*Bull. Soc. Chim.*, Series 3, vol. xxix., p. 301.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, June 4th, 1903.

Dr. W. H. Perkin, F.R.S., Vice-President, in the Chair.

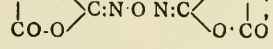
Certificates were read for the first time in favour of Messrs. Ernest Derwent, 36, Sixth and Railroad, Ironton, Ohio, U.S.A.; William Forster, 6, North Railway Street, Seaham Harbour; Edwin Reginald Hughes, 106, Queen Victoria Street, London, E.C.; Walter Ernest Jennings, 8, Rawdon Terrace, Ashby de la Zouch; William Parry, B.Sc., 23, Mount Pleasant, Waterloo, Liverpool.

The following certificate was authorised by the Council under By-law I. (3):—Wilfrid William Ogilvy Beveridge, A.M.S. Laboratory, Pretoria.

Of the following papers, those marked * were read:—

*83. "*Formation of an Anhydride of Camphoryloxime.*" By T. M. Lowry.

When nitrocamphor is boiled with concentrated hydrochloric acid, the greater part of the substance passes into solution, and is converted into camphoryloxime. During the investigation of this isomeric change (*Trans.*, 1898, lxxiii., 1002), a considerable quantity of a resinous by-product was accumulated; this substance has now been examined and found to contain an *anhydride*,—



of *camphoryloxime*, which, after crystallisation from alcohol, softens at about 215°, melts at 220°, and has $[\alpha]_D = +26°$ in acetone.

*84. "*Mutarotation of Glucose as Influenced by Acids, Bases, and Salts.*" By T. M. Lowry.

Both acids and bases have an accelerating effect on the mutarotation of glucose, whilst potassium chloride is without influence. If the mutarotation is conditioned by the presence in the glucose of an exceedingly minute quantity of basic impurity or a somewhat larger amount of acid impurity, a retardation should be produced when the base or acid is neutralised by adding hydrogen chloride or potassium hydroxide respectively. Careful quantitative experiments showed that this retardation does not occur, and the conclusion is drawn that although the mutarotation is accelerated by both acids and bases, its occurrence is independent of the presence of these impurities. Probably the water alone is sufficient to condition the change if enough impurity is present to render it an electrolyte.

*85. "*The Solubility of Dynamic Isomerides.*" By T. M. Lowry.

Whilst the rotatory power affords a general method for studying the dynamic isomerism of optically active substances, no similar method is available in the case of inactive bodies. The measurements of electrical conductivity, so effectively employed by Hantzsch in the study of pseudo-acids, pseudo-salts, and pseudo bases, can only be made when one of the isomerides is an electrolyte and at least moderately soluble in water. Of the other physical properties, density, molecular solution volume, refractive index, dispersion, and magnetic rotatory power differ relatively little in isomeric compounds, and the melting point, colour, and ultra-violet absorption cannot easily be made the basis of quantitative measurements. The solubility of dynamic isomerides is, however, usually very different, and under certain conditions it is possible to follow experimentally the gradual change of solubility as a substance is converted into a dynamic isomeride. This method, which has been devised and tested in the case of optically active substances, will, it is believed, be of service in the study of inactive bodies, and thus render possible the quantitative examination of many changes that have hitherto been examined only qualitatively.

If the less soluble isomeride is initially in contact with the solvent, the solubility gradually increases until the liquid phase contains a normal proportion of the two forms. If, however, the more soluble isomeride is used, the solubility increases until the liquid is saturated with both forms; the solution then contains a much greater proportion of the more soluble isomeride, and isomeric change proceeds continuously, the more soluble modification dissolving whilst the less soluble form separates from the solution; finally, when the whole of the more soluble form has dissolved, the solubility decreases to a constant value identical with that obtained when the less soluble isomeride alone is used.

Measurements of the solubility of pseudo-*8*-bromonitrocamphor in benzene show that at 10° the solubility gradually increases from 2·3 to 9·3 grms. per 100 grms. of benzene, whilst when both forms are present in the solid phase the solution contains nearly 14 per cent of the substances.

*86. "*The Rusting of Iron.*" By G. T. Moody.

The contention of Dunstan (*Proceedings of the Royal Artillery Institution*, 1899, No. 5, xxvi.; *Proc.*, xix., p. 150) that carbon dioxide is not essentially concerned in the process of rusting, and that this change is caused by hydrogen peroxide is based on the observation that solutions of chromium trioxide, potassium dichromate, potassium ferrocyanide, sodium nitrite, and other substances which decompose hydrogen peroxide, entirely or nearly entirely prevent rusting. The author finds that the retarding action exercised by these substances is due to the influence they exert on the absorption of carbon dioxide. For example, when exposed to the gas under exactly the same conditions, water absorbed 90·6 volumes, whilst a 15 per cent solution of chromium trioxide and a 20 per cent solution of sodium nitrite absorbed 4·2 volumes and 5·6 volumes respectively. A solution of chromium trioxide—which itself does not attack iron—appears all the more to exert a protecting influence because of the ease with which it dissolves ferric oxide. Iron, when placed under a one per cent solution of chromium trioxide exposed to air, remains bright for some weeks, although the metal is slowly passing into solution. Eventually rust commences

to form on the metal, although the solution still contains free chromic acid.

When iron is exposed to water and oxygen previously freed as far as possible from carbon dioxide, the volume of oxygen remains practically unchanged. On admitting carbon dioxide, the volume of oxygen diminishes rapidly, and rusting becomes visible.

The interaction of iron with aqueous carbonic acid appears to be strictly comparable with that occurring between iron and sulphuric acid. A solution of carbonic acid, formed by saturating 2·4 litres of water at 18° with carbon dioxide, when left in contact with 500 grms. of clean iron turnings, yielded 635 c.c. of hydrogen in seven days. After remaining for one week, the solution contained 0·1 per cent of iron present as ferrous bicarbonate, a substance which is readily decomposed by atmospheric oxygen yielding a mixture of ferrous carbonate and ferric oxide, whilst a part of the carbonic acid is regenerated. On account of the case with which this change takes place, it follows that in presence of oxygen a definite weight of carbonic acid will exert a greater corroding influence on iron than will its equivalent of sulphuric or hydrochloric acid.

The author contends that the primary action in rusting involves the interaction of iron and acid, and that rust is formed by the subsequent oxidation of ferrous salt.

Discussion.

Mr. C. E. Groves said it was known that iron immersed in potassium carbonate solution did not rust, and asked whether the author had examined the action on iron of a solution of *potassium* hydrogen carbonate saturated with carbon dioxide. He believed it was not generally known that solid caustic potash containing about 5 per cent of water, when fused at a gentle heat in contact with steel, readily attacked it, the iron apparently forming a ferrous compound. Fused caustic soda, however, had practically no action on iron.

Dr. Jowett said that, having co-operated with Prof. Dunstan in the work to which Dr. Moody had referred, he must point out that much of the criticism seemed to be based on a misunderstanding. The rusting of iron was the sum of several chemical reactions each of which had been separately studied. It was not stated or thought that the oxidation in which hydrogen peroxide might take part constituted the whole phenomenon of rusting, and one of the experiments shown by Dr. Moody, namely, the evolution of hydrogen from a mixture of aqueous carbonic acid and iron, was referred to in Prof. Dunstan's note. The oxidation in which it was suggested that hydrogen peroxide was involved, occurred when oxygen, water, and pure iron were used, and it was a fact that substances which decomposed hydrogen peroxide prevented oxidation under conditions similar to those in which the peroxide was produced during the oxidation of zinc.

Finally, although the analyses of rust produced under ordinary atmospheric conditions generally showed the presence of carbon dioxide, they agree closely with the formula $Fe_2O_2(OH)_2$, which was also found to represent the composition of the product formed by the oxidation of iron under the conditions previously mentioned.

Dr. Scott asked if the chromic acid was free from sulphuric and nitric acids.

He mentioned that Dr. Russell's experiments on the action of various metals on photographic plates showed that zinc very readily gave hydrogen peroxide and even mercury containing 1/300th per cent of zinc produced sufficient to affect a photographic plate.

Dr. Kohn asked whether any experiments had been tried on the influence of light on the action of carbonic acid, since many changes effected by air and moisture and attributed to the formation of hydrogen peroxide did not occur or were diminished in absence of light. Such experiments might indicate whether hydrogen peroxide had any contributory action.

Mr. A. C. Chapman asked whether Dr. Moody had assured himself that the amount of hydrogen evolved in the experiment referred to was not greater than that which would correspond with the carbon dioxide present, and also whether he had made any experiments as to the influence of the purity of the iron employed on the quantity of gas evolved. In other words, was the hydrogen solely the result of replacement, or might not some of it have been produced by electrolytic action pure and simple.

Dr. Henry pointed out that in the course of the experiments referred to in Prof. Dunstan's note, a specimen of pure sheet iron with bright surfaces had been immersed for more than six years in a 4 per cent aqueous solution of chromic acid contained in a loosely stoppered jar; during the whole of that time the surfaces had remained perfectly bright, and there was no evidence of either the reduction of the chromic acid or the formation of iron rust, although the solution was in contact with atmospheric carbon dioxide. He suggested that the rusting observed by the author when iron was kept in solutions of dilute chromic acid in presence of carbon dioxide might be due to the employment either of commercial iron or chromic acid containing impurities; it was known that the presence of neutral salts such as sodium chloride in water in which iron was immersed accelerated the rate of rusting.

Dr. Lowry said that if hydrogen peroxide were a product of the initial stage in the rusting of iron, its destruction by chromic acid might be expected to assist rather than retard the oxidation.

Dr. Moody, in reply, said that in discussing this subject it was necessary to be agreed as to what was meant by rusting. He understood rusting to mean the corrosion taking place when metals were left exposed to air under ordinary conditions. Water condensed from air contains carbonic acid, which in contact with iron immediately gives rise to a ferrous salt. Since ferrous salts equally with chromic acid, sodium nitrate, and potassium ferrocyanide establish a condition in which the production of hydrogen peroxide is inhibited, it follows that the theory advanced by Dunstan can have no bearing on the atmospheric rusting of iron.

87. "*Imino-ethers Corresponding with Ortho-substituted Benzenoid Amides.*" By G. D. Lander and F. T. Jewson.

Pinner's method of synthesis of imino-ethers fails either partially or completely with aryl cyanides containing an *ortho*-substituent, and one of the authors has shown that the main product of the action of ethyl iodide and dry silver oxide on *o*-toluamide in boiling alcoholic solution is a nitrile (*Trans.*, 1901, lxxvii., 695).

When boiling alcohol is employed as a medium, the alkylation of other amides by this method seems to be characterised by the formation of nitriles, but whilst the yield of imino-ether from *o*-toluamide is only 13·6 per cent, the proportion is 70 per cent in the case of *p*-toluamide; this result is explained by supposing that the *o*-compound more readily loses alcohol than its *p*-isomeride, $C_7H_7.C:NH\cdot OEt = C_7H_7\cdot CN + EtOH$. The same constitutive factor, however, renders the *o*-imino-ether more stable as regards hydrolysis by aqueous hydrochloric acid, $C_7H_7C:NH\cdot OEt + H_2O + HCl = C_7H_7\cdot CO_2Et + NH_4Cl$.

Although better yields of the imino-ether are obtained when the synthesis is carried out in boiling ethereal solution, yet in this case nitrile is also produced.

The *hydrochloride* of *o*-chlorobenziminoethyl ether decomposes at 105°, yielding *o*-chlorobenzamide; the *methyl* analogue forms a *hydrochloride* which decomposes at about 110°. o *Chlorobenzmethylamide* is also a product of the methylation of *o*-chlorobenzamide, and forms colourless needles melting at 92—94°. o-*Toluiminomethyl ether* was prepared by the action of methyl iodide on the silver derivative of *o*-toluamide; its *hydrochloride* decomposes between 110° and 115°. o-*Toluiminoethyl ether*, when mixed with nitrile, distils without change between 106° and 118° under 20—25 m.m. pressure, and yields a *hydrochloride* which decomposes at 105—106°.

88. "*The Hydrolysis of Ethyl Mandelate by Lipase.*" By H. D. DAKIN.

Optical isomerides are frequently very differently affected by enzymes as well as by living organisms, but the production of an optically active substance from inactive material as the result of simple enzyme action has not hitherto been conclusively demonstrated.

If the conception of an enzyme as an optically active asymmetric complex is correct, and, moreover, if combination occurred between the enzyme and the substance acted on, it should be possible to show that when an enzyme acts on an optically inactive substance, the two optical components are decomposed with unequal velocity.

This was shown to be the case when inactive ethyl mandelate was hydrolysed by the enzyme lipase. In all cases, provided hydrolysis was incomplete, the separated mandelic acid was found to be strongly dextrotatory whilst the unchanged ester was lævorotatory.

The reaction would appear to bear a close analogy to the hydrolysis of esters prepared from an optically active alcohol and an inactive acid (Marckwald and McKenzie, *Ber.*, 1901, xxxiv., 469).

89. "*Isomeric Change in Benzene Derivatives. The Conditions Influencing the Interchange of Halogen and Hydroxyl in Benzenediazonium Hydroxides.*" By K. J. P. ORTON.

The supposed *s*-tribromophenylnitrosoamine, obtained by Hantzsch and Pohl (*Ber.*, 1902, xxxv., 2964) from *s*-tribromobenzenediazonium acetate under conditions which, according to the author's earlier investigations (*Proc. Roy. Soc.*, 1903, lxxi., 153), are favourable to the replacement by hydroxyl of the bromine atom in the ortho-position relatively to the diazo-group, is now shown, by an exact repetition of Hantzsch and Pohl's experiments, to consist of a mixture of 3 : 5-dibromo-*o*-quinonediazide (3 : 5-dibromo-*o*-diazophenol) and an amorphous condensation product, probably a hydroxyazo-derivative, either when prepared from the diazonium salt or from the corresponding alkali diazo-oxide (diazotate). Moreover, the hydrochloride obtained by Hantzsch and Pohl by passing hydrogen chloride into an ethereal solution of the original yellow material, and thought by them to be the hydrochloride of the nitrosoamine, is, in fact, the hydrochloride of the quinonediazide, which can readily be prepared from it by hydrolysis with water.

The transformation of the diazonium acetates derived from 2 : 4 : 6-tribromo-3-nitroaniline, 2 : 3 : 4 : 6 tetrabromoaniline, 3 : 5-dibromo-*p*-toluidine, 2 : 6-dibromoaniline, 2 : 4-dichloroaniline, and 2 : 4-dibromo-5-nitro aniline have been examined. When a nitro-group is in the meta-position relatively to the diazo-group, the replacement of the *o*- or *p*-bromine atom by hydroxyl takes place very readily, the diazo-compound in this respect resembling the naphthalene derivatives (*Proc.*, 1902, xviii., 252). It is remarkable that 3 : 5-dibromo *p*-toluenediazonium acetate does not lose bromine.

2 : 6 Dibromobenzenediazonium acetate slowly undergoes this change, but chlorine ions are scarcely appreciable in a solution of 2 : 4-dichlorobenzenediazonium acetate, even after several days. Bromine is, however, rapidly displaced when a nitro-group is in the meta-position relatively to the diazo-group, as in the 2 : 4-dibromo-5-nitrobenzene diazo-compounds.

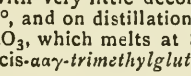
This interchange takes place not only with the diazonium acetates and hydrogen carbonates, but also in a similar manner with the salts of other weak acids, such as the cyanides and the nitrites, but with these salts, however, other reactions occur simultaneously, thus 2 : 4 : 6-tribromo-1-nitrobenzene is also formed from the nitrite.

When the diazonium salt is present as sulphate, the change is extremely slow at the ordinary temperature, but at 80° nearly one atomic proportion of bromine is eliminated in four hours, a fact which no doubt accounts for the apparent impossibility of obtaining *s*-tribromophenol by heating aqueous solutions of *s*-tribromobenzenediazonium salts.

The following substances were described :—2 : 4 : 6-*tribromobenzeneazo-β-naphthol*, melting at 173—174°; 3 : 5-*dibromophenol-2-azo-β-naphthol*, copper-coloured plates melting at 214—215°; 3 : 5-*dibromo-2-nitro-p-quinonediazide* (3 : 5 *dibromo-2-nitro-p-diazophenol*), prepared from 2 : 4 : 6-tribromo-3-nitroaniline, crystallises in yellow plates decomposing at 196°; *tribromoquinonediazide* (*tribromodiazophenol*), prepared from 2 : 3 : 4 : 6-tetrabromoaniline, forms orange crystals melting and decomposing at 124°; 3-*bromo-o-quinonediazide* (3-*bromo-o-diazophenol*), prepared from 2 : 6-dibromoaniline, crystallises in orange needles melting and decomposing at 103°; 2 : 4-*dichlorobenzeneazo-β-naphthol*, scarlet prisms melting at 190°; *chlorophenolazo-β-naphthol*, minute needles melting at 265°; 3 : 5-*dibromo-p-tolueneazo-β-naphthol*, scarlet prisms melting at 141°.

90. "*The Synthesis of αα'γ-Trimethylglutaric Acid, of the* cis- *and* trans-*Modifications of β-Hydroxy-αα'γ-trimethylglutaric Acid, and of αα'γ Trimethylglutaconic Acid.*" By W. H. PERKIN, jun., and ALICE E. SMITH.

A mixture of ethyl dimethylmalonate and ethyl acetate is readily acted on by sodium, yielding the sodium compound of ethyl αα-dimethylacetonedicarboxylate, $CO_2Et{\cdot}CMe_2{\cdot}CO{\cdot}CHNa{\cdot}CO_2Et$, and if this is treated with methyl iodide, *ethyl αα'γ-trimethylacetonedicarboxylate*, $CO_2Et{\cdot}CMe_2{\cdot}CO{\cdot}CHMe{\cdot}CO_2Et$, is produced as a nearly colourless oil boiling at 195—197° under 100 m.m. pressure, which, in alcoholic solution, gives a violet coloration with ferric chloride. When this ester is reduced with sodium amalgam, it yields a mixture of the *cis*- and *trans*-modifications of *β-hydroxy-αα'γ-trimethylglutaric acid*, $CO_2H{\cdot}CMe_2{\cdot}CH(OH){\cdot}CHMe{\cdot}CO_2H$. The *trans*-acid melts at 155°, and when rapidly heated under reduced pressure distils with very little decomposition. The *cis*-acid melts at 115°, and on distillation yields a crystalline substance, $C_8H_{10}O_3$, which melts at 88°, and is probably the anhydride of cis-*αα'γ-trimethylglutaconic acid*,—



Both the *cis*- and *trans*-modifications of the hydroxy-acid, when treated successively with phosphorus pentachloride and diethylaniline, or when digested with fuming hydriodic acid, are converted into trans-*αα'γ-trimethylglutaconic acid*; this acid, which melts at 150°, and, when heated in small quantities, volatilises to a certain extent without decomposition, is reduced with difficulty, but by the action of a large excess of alcohol and sodium becomes converted into *αα'γ-trimethylglutaric acid*, $CO_2H{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H$, melting at 98°. When subjected to the action of dry bromine vapour, *trans αα'γ*-trimethylglutaconic acid is converted into *βγ-dibromo-αα'γ-trimethylglutaric acid*, which crystallises from formic acid, and melts at 205—207°.

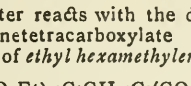
91. "*Hexamethyleneoctocarboxylic Acid and the* cis- *and* trans-*Modifications of Hexamethylenetetracarboxylic Acid* (*Hexahydropyromellitic Acid*"). By T. W. D. GREGORY and W. H. PERKIN, jun.

When ethyl propanetetracarboxylate,—

$$(CO_2Et)_2CH{\cdot}CH_2{\cdot}CH(CO_2Et)_2,$$

is treated with bromine, it yields *ethyl dibromopropanetetracarboxylate*, $(CO_2Et)_2CBr{\cdot}CH_2{\cdot}CBr(CO_2Et)_2$, which melts at 55°.

This bromo-ester reacts with the disodium compound of ethyl propanetetracarboxylate giving an almost quantitative yield of *ethyl hexamethyleneoctocarboxylate*,—



a colourless, crystalline substance (m. p. 46°), which, when digested with hydrochloric acid, yields the free *hexamethyleneoctocarboxylic acid*; this substance decom-

poses at 218°, giving rise to the *cis*- and *trans*-modifications of *hexamethylenetetracarboxylic acid*,—

$$\begin{array}{l} CO_2H\cdot CH\cdot CH_2\cdot CH\cdot CO_2H \\ \quad\quad\quad\quad | \quad\quad\quad | \\ CO_2H\cdot CH\cdot CH_2\cdot CH\cdot CO_2H \end{array}.$$

The *cis*-acid melts at 140°, and its *anhydride* at 60; the *trans*-acid melts at 175°, and yields the latter compound on digestion with acetic anhydride and subsequent distillation.

92. "*The Bases contained in Scottish Shale Oil.*" Part II. By F. C. GARRETT and J. A. SMYTHE.

The only bases obtained in a state of purity from the fractions of Scottish shale oil boiling between 164° and 180° are 2 : 3-*dimethylpyridine* and 2 : 4 : 6-trimethylpyridine. The lower homologue, which has not been described, is a liquid lighter than, and insoluble in, water, having a pleasant aromatic smell, and boiling at 163—164° under 768 m.m. pressure. Its mercurichloride melts at 120°, and its aurichloride at 96°; its platinichloride melts and decomposes at 216°. The trimethylpyridine boils at 171° under 768 m.m. pressure, and gives an aurichloride containing one molecule of water of crystallisation, and melting at 53°; when anhydrous, the salt melts at 112°.

93. "*A Direct Method for Determining the Latent Heat of Evaporation.*" By J. CAMPBELL BROWN.

The latent heats of thirteen alcohols, seven acids, and twenty-eight esters have been directly determined by means of an apparatus adapted for ascertaining the weight of liquid evaporated by a determinate amount of heat applied at the boiling-point of the substance, when this is surrounded by a double jacket containing its own vapour.

94. "*Isomeric partially Racemic Salts containing Quinquevalent Nitrogen.* Part X. *The Four Isomeric Hydrindamine d-Chlorocamphorsulphonates*, $NR_1R_2H_3$." By F. S. KIPPING.

The isomeric partially racemic α- and β-salts obtained from *dl* hydrindamine and *d* chlorocamphor-sulphonic acid (*Trans.*, 1900, lxxvii., 889) are not resolved into their components under conditions similar to those employed in the resolution of the corresponding bromo-salts (*Proc.*, 1902, xviii., 209), but the four isomeric salts of the type $NR_1R_2H_3$, from which the partially racemic compounds are formed, have been isolated and examined.

d-Hydrindamine, prepared from the pure αd-bromo-salt (previously denoted αA-salt, *Proc., loc. cit.*), combines with *d*-chlorocamphorsulphonic acid, giving rise to two isomeric salts, one of which is formed in relatively very small quantities. The principal product, which corresponds with the αd-bromo-salt and is distinguished as the αd-isomeride, is easily obtained in a pure condition; it separates from water in well-defined, compact, hydrated crystals, melts at 208—209°, and has a specific rotation $[\alpha]_D = +46°$ in aqueous and $+15{\cdot}5°$ in chloroform solution. It differs greatly in outward properties from the corresponding αl-salt of the bromo-acid, and also from all the other three isomeric chloro-salts.

The second product, which corresponds with the βd-bromo-salt (previously denoted βA-salt), is only obtained in a pure condition after a long course of fractional crystallisations; it separates from water in long, hydrated needles, melts at 202—203°, and its specific rotation in aqueous solution is $[\alpha]_D = +59°$, the value in chloroform being $[\alpha]_D = +50°$.

The great difference between these isomerides is very noteworthy considering the fact that the corresponding bromocamphorsulphonates of hydrindamine and of methylhydrindamine (Tattersall and Kipping, *Proc.*, xix., p. 145) are so similar that the βd-isomeride cannot be obtained in a pure state.

The pure αd-hydrindamine chlorocamphorsulphonate, decomposed with barium hydroxide solution, gives both the αd- and the βd-isomerides when regenerated from its component acid and base, a proof that these two salts are formed from structurally and optically identical components.

-Hydrindamine, prepared from the pure al-modification (previously denoted αB) of the bromo-salt, also combines with *d*-chlorocamphorsulphonic acid, giving rise to a mixture of very unequal quantities of two isomeric salts. The principal product, the al-modification, corresponding with the al-bromo-salt, separates from water in long, anhydrous needles, indistinguishable in appearance from those of the al-bromo-compound; it melts at 118—119°, and has a specific rotation $[\alpha]_D = +44°$ in aqueous and $+45{\cdot}5°$ in chloroform solution. The subsidiary product, namely, the βl-isomeride (formerly denoted βB), is only separated in a pure condition with very great difficulty; it crystallises from water in long, anhydrous needles which generally melt at about 140—145°, the indefinite melting-point being apparently due to dimorphism, as in the case of the corresponding bromo-isomeride. Its specific rotation is $[\alpha]_D = +57{\cdot}5°$ in aqueous and $+60{\cdot}5°$ in chloroform solution.

When the pure al chloro-salt is decomposed with barium hydroxide solution and then regenerated from its own acid and its own base, a mixture of the al- and βl-isomerides is obtained, just as from the original *l* base.

It is to be noted that the βd- and βl-chloro-salts have a much *higher* molecular rotation than that of *d*-chlorocamphorsulphonic acid, whereas in the case of the corresponding bromo-salts the position is reversed; it follows, therefore, that the formation of these isomerides cannot be attributed to any partial racemisation of the acid or the base.

The isolation of these four isomeric hydrindamine *d*-chlorocamphorsulphonates seems to afford the final proof that the author's explanation of the existence of the partially racemic α- and β salts is the true one (*Trans., loc. cit.*).

95. "*Isomeric Compounds of the Type* $NR_1R_2H_3$." By F. S. KIPPING.

The isolation of the four isomeric hydrindamine *d*-chlorocamphorsulphonates (see previous abstract), the proof of the existence of four isomeric methylhydrindamine bromocamphorsulphonates (derived from one *dl*-base) (Tattersall and Kipping, *Proc.*, xix., p. 145), and other evidence fully confirm the author's views as to the nature of the isomeric partially racemic salts which have been previously studied (Kipping, *Trans.*, 1900, lxxvii., 861; 1901, lxxix., 430), and establish the occurrence of isomerism in compounds of the type $NR_1R_2H_3$ (*Proc.*, 1902, xviii., 211).

The stability of the isomeric salts in aqueous solution leads to the conclusion that there are two different ions NR_1H_3- for each optically active base, and, consequently, it should be possible to transfer such ions from one acid to another without altering the configurations particular to them. Experiments bear out this conclusion. The partially racemic β-salt of hydrindamine and *d*-bromocamphorsulphonic acid is not converted into the corresponding α-salt when it is repeatedly evaporated first with concentrated hydrochloric acid, and then with water, or when it is successively treated in aqueous solution with sodium carbonate and hydrochloric acid, the solution being then evaporated. The four basic ions of the β-salt can thus be transferred from the bromo-acid to hydrochloric acid or to carbonic acid, and back again to the bromo-acid without altering their relative proportions as long as the base is never in the free state.

The platinichlorides, prepared from the ad-, al-, and βl-modifications [previously called the αA-, αB-, and βB-modifications respectively (*Proc.*, 1902, xviii., 209)] of hydrindamine *d*-bromocamphorsulphonate by precipitating in presence of hydrochloric acid, seem to be identical in outward properties, and the hydrochlorides obtained from the platinichlorides by decomposing with hydrogen sulphide are also indistinguishable in appearance and in melting-point; it would seem, nevertheless, that each of the optically active hydrindamines gives rise to two different

hydrochlorides (indistinguishable in ordinary properties), firstly, because of the behaviour of the partially racemic β-salt (see above), and, secondly, because the βl-modification of hydrindamine *d*-chlorocamphorsulphonate can be converted into a hydrochloride from which the original βl-salt is obtained on evaporating with the chloro-acid.

The hydrochloride, prepared from the above-mentioned βl-bromo-salt, gave with ammonium *d*-bromocamphorsulphonate what appeared to be the pure βl isomeride, but on repeating the experiment under different conditions, starting from the βl-chloro-salt, the αl modification was obtained; further investigation is necessary before this difference in behaviour can be explained, but it seems reasonable to conclude that *four isomeric hydrochlorides* of hydrindamine are capable of existence.

The molecular rotations of the αd- and αl-salts in dilute aqueous solution are in all cases practically normal, but the βd- and βl-hydrindamine bromocamphorsulphonates give values which are far too low, whereas the βd- and βl hydrindamine chlorocamphorsulphonates give numbers which are far too high; molecular weight determinations in boiling aqueous solution seem to indicate that the salts of the β-series are not so highly dissociated as the corresponding α-salts, but the evidence is very inconclusive.

The existence of isomeric salts of the type $NR_1R_2H_3$ can be accounted for by assuming that the five valencies of the nitrogen atom are directed from the centre to the angles of a square-based pyramid, but in view of the highly conflicting experimental evidence bearing on the question of the configuration of the nitrogen atom, this subject cannot yet be profitably discussed; even in the case of trivalent nitrogen, there is great uncertainty, as no case is yet known of isomerides of the type $NR_1R_2R_3$, although the existence of such compounds is a probable, if not a necessary, consequence of the hypothesis of Hantzsch and Werner.

PHYSICAL SOCIETY.

Ordinary Meeting, June 5th, 1903.

Dr. R. T. Glazebrook, F.R.S., President, in the Chair.

The Meeting was held, by invitation of Prof. Trouton, in the Physical Laboratory, University College.

Prof. Rutherford read a paper on "*Radio-active Processes.*"

There are three distinct types of radiation spontaneously emitted from radio-active bodies, which may be called the α, β, and γ rays. The α-rays are prominent in causing the conductivity of a gas, they are easily absorbed by metals, and are projected bodies, not waves. These bodies are about the size of a hydrogen atom, they are positively charged and travel with about one-tenth of the velocity of light. The β-rays are similar in all respects to the cathode rays produced in a vacuum tube. The γ rays are probably like Röntgen rays, but of very great penetrating power. The α-rays are by far the most important. In addition to these rays, two of the radio-elements give off radio-active "emanations," which are in all respect like gases. The radiations from these emanations are not permanent, but fall off in a geometrical progression with the time. The radiation of the thorium emanation falls to half value in one minute, that from radium in four days. They have all the properties of gaseous matter in infinitesimal quantity. Their coefficients of diffusion can be measured, the order of their molecular weights is 100, they are occluded by solid compounds producing them, and may be condensed at low temperatures. The radium emanation condenses sharply at $-150°$ C., the thorium emanation between $-120°$ C. and $-150°$ C. The two emanations excite on objects with which they come in contact two kinds of temporary radio-activity, that from the radium emanation decaying much faster than that from the thorium emanation. The latter decays in a G.P. with the time falling to half value in eleven hours. These effects appear to be produced by solid matter in invisible and unweighable quantity, which can be dissolved off in some acids, but not in others. On evaporating the solutions, the radio-activity is obtained unchanged in the residue. The experiments of Crookes and Becquerel in separating by chemical treatment the matter responsible for the activity of uranium, called uranium X, were referred to, together with the latter's observation that the separated activity had completely decayed after the lapse of a year, by which time the uranium itself had completely recovered its activity. The work of Rutherford and Soddy on thorium was then discussed in detail. Thorium precipitated in solution by ammonia retains only 25 per cent of its activity. If the solution is evaporated and ignited, the remaining 75 per cent is found in the extremely small residue left, which, by reason of its separation, is different chemically from thorium, and was called Thorium X. Left to themselves, the thorium gradually recovers its activity and the ThX loses it. The activity of the latter falls in a G.P. with the time, the half value being reached after four days. At any time the sum-total of the two activities is a constant. This would occur if the ThX were being continually produced by the thorium, and this was shown to be the case by precipitating thorium at definite intervals after its separation from ThX. The ThX, and not thorium, produces the thorium emanation. The production of ThX by thorium, of the emanation by ThX, and of the matter causing the excited activity by the emanation, are all changes of the same type, although the rates of change are distinct in each case. The change of uranium into uranium X is also similar, being the slowest of all. Twenty-two days elapse before uranium freed from ThX recovers one-half of its activity. In radium, the radium emanation is the first product produced, and since this in a solid is almost completely occluded, the activity of a radium salt after it has been obtained from its solution rises after precipitation to several times its original value, due to the occlusion of the emanation. In all three radio-elements a part of the radio-activity is non-separable, and this part consists only of α-rays. The β-rays only result at the last stages of the process that can be experimentally traced. In all cases the radiation, from any type of active matter, is a measure of the amount of the next type produced. Thus the radio-activity of ThX at any period throughout its life is always a measure of the amount of emanation it produces. These results find their explanation if it is supposed that the α particles projected form integral portions of the atom of the radio-active element. Thus, ThX is thorium minus one or more projected α particles. The emanation, similarly, is ThX less a further α particle, and so on. The non-separable activity is due to the atoms of the original radio-element disintegrating at a constant rate. The whole of the processes take place unaltered in velocity, apparently under all conditions of temperature, state of aggregation, and chemical combination. This is to be expected of a sub atomic change in which one system only is involved at each change. On this view, the spontaneous heat-emission of solid radium salts, discovered by Curie, is explained by the internal bombardment by the α particles shot off and absorbed in the mass of the substance. The amount of energy given out in these sub-atomic changes is enormous, and from Curie's experiments it can be deduced that each grm. of radium gives out 10^9 grm.-calories during its life, which is sufficient to raise 500 tons a mile high. It seems probable that the internal energy of atoms in general is of a similar high order of magnitude.

Sir Oliver Lodge congratulated Prof. Rutherford and Mr. Soddy upon the field of research which had opened up to them, and upon the way they were pursuing it. Referring to the fact that the temperature of a piece of radium is above that of its surroundings, he said that Prof. Rutherford's discovery that atoms of matter were thrown out by radium at one-tenth the speed of light

would account for energy-effects, and he thought it necessary that when energy passed from an unrecognised atomic to an irregular molecular form, that previously non-existent heat would be produced. The important point in Prof. Rutherford's work was that he had established the fact that one kind of matter is thrown off by another kind of matter, and had also measured the velocity and weight of the particles thus thrown off. We were accustomed to electrons being shot out by matter, but the proof that light atoms are thrown off from heavy atoms was the evolution or transmutation of matter experimentally demonstrated. The heavy atoms of radium appear to collapse and throw off atoms of low atomic weight; the remainder is unstable, and more matter is thrown off, the original atom getting, it is to be presumed, lighter and lighter—according to the view of the author of the paper. It might be thought that this hypothesis about the degradation and the instability of the atoms was mere speculation, but it was the most reasonable explanation of observed phenomena. And the reason he was thus cordially willing to accept it as a working hypothesis was because he had been indistinctly looking for some such effect, being guided thereto by pure theory. And that was the chief point he wished to bring forward.

According to an electric theory of matter, *i.e.*, on the view that an atom contained electrons with rapid interatomic movements obeying laws like astronomical laws, this instability ought to exist. Taking a formula by Prof. Larmor for the radiating power of an accelerated electric charge, Sir Oliver Lodge gave a rough proof of the latter statement (reproduced in *Nature* for June 11th). He stated, in conclusion, as a working hypothesis, that we must not suppose that atoms are permanent and eternal, and suggested that we may possibly find a rise and decay in ordinary matter, and find that the history of an atom may be written—in accordance with the analogy of solar systems and cosmic configurations generally. On the electric theory of matter, the falling together of electrons might produce the electric aggregate called an atom, and its subsequent gradual decay or separation into other forms would be accompanied by epochs of radio-activity.

Prof. W. E. AYRTON, after congratulating the author, said he would like to ask a question. Prof. Rutherford had shown us the discharge of an electroscope when a thick plate of metal was placed between a piece of radium and the instrument. Would the electroscope be affected if a piece of radium *completely* surrounded by an earthed *metal* casing was brought near to it? Again, if a piece of radium was insulated inside a completely closed metal box, would an electroscope, metallically connected with the outside of the box—the whole being placed in a very good vacuum—be charged, and if so, what would be the sign of the charge?

Prof. EVERETT found it difficult to believe that there was a sufficient store of energy in the atom to account for the effects observed. He asked if the phenomena were not due to resonance, the radium atoms being shaken asunder by vibrations in the ether to which they were responsive. These scattered atoms might knock asunder some of the atoms of neighbouring bodies, and so produce the β-rays.

Prof. S. P. THOMPSON pointed out that the notion of energy within the atom was based upon the statement that the temperature of a piece of radium was above the temperature of its surroundings. Without doubting the work of Curie, he thought that critical experiments should be made on this point before it could be looked upon as an accepted fact, or such large generalisations be based upon it.

Dr. LOWRY called attention to the slender evidence on which the theory of atomic degradation had been based. The behaviour of thorium and ThX was precisely analogous to that of a substance like π-bromonitrocamphor, which exists in an inactive "normal" form as a neutral substance and a dielectric, but also in an active "pseudo" form, in which it is a strong acid and an electrolyte. Both forms are fairly stable in the solid state, but when dissolved are exceedingly labile, and the merest trace of impurity is sufficient to bring about an isomeric change which leads in the course of a few days or hours to a condition of equilibrium in which there are about 94 parts of the inactive normal to 6 parts of the active pseudo form. The curves representing the rate of recovery and decay of (electrolytic) activity are mathematically identical with those shown for the recovery and decay of radio-activity by the two modifications of thorium and uranium. There is, therefore, the strongest evidence in favour of the view that the conversion of thorium into ThX is a *reversible change*, and that the emanations and excited activity are merely physical phenomena.

Prof. RUTHERFORD, in reply to Prof. Ayrton, said that in the first case discharge would take place, and that the result in the second case would depend upon the thickness of the walls, and therefore upon the nature of the rays which could pass through. He also pointed out that Dr. Lowry's explanation involved him in perpetual motion. It did not explain radio-activity, and it was difficult to see how it could account for the phenomena occurring in stages. Moreover, there was no reversible chemical action that went on at the same rate at a red heat as in liquid air. With regard to Prof. Everett's suggestion, it seemed that such a process would be even more wonderful than that suggested. The phenomena go on unchanged even when the substance is shielded from external influence by many inches of lead. He felt confident that Curie's observation of heat emission would prove to be well founded.

NOTICES OF BOOKS.

Tables for Students of Quantitative Chemical Analysis. Drawn up by CHARLES E. FAWSITT, Ph.D., B.Sc. Edinburgh: W. F. Clay. 1903. Pp. 23.

THE tables given in this publication appear to be very similar to, if not identical with, those given in the appendices of many text-books. They consist principally of two or three examples of the calculation of results, a table of atomic weights, four pages of logarithms, and a table of formula weights, factors, and percentages, arranged in alphabetical order of substances. They are set out in a convenient manner, and will be handy to have in the laboratory.

Annual Reports. By E. MERCK. Complete Series, Vol. XVI., 1902. Darmstadt. May, 1903. Pp. 209.

MERCK'S reports are so well known by now that it needs very few words to recall their usefulness and value. The one now before us deals with the latest advancements of pharmaceutical chemistry and therapeutics; the greater part is devoted to preparations, more especially the new ones, particulars of which are collected annually from medical papers throughout the world, and collated and epitomised for this Report by the Scientific Department at the Darmstadt works. By this means physicians and pharmacists are saved the trouble of referring to original sources. Among these notes there is an interesting one on radio-active substances and their dermato-therapeutic action in cases of lupus. The radio-active substance used was a whitish powder, being a mixture of barium chloride and radium chloride, and possessing a radio-active power 5200 to 19,000 times greater than that of uranium. The Report contains also a complete bibliographical index, as well as others for authors' names, diseases and symptoms, and a general index.

Sulphurised and Nitrated Compounds Derived from Sulphide of Carbon; Additions.—Marcel Delépine. In this paper the author describes the action of the acids on the nitro-substituted imidodithiocarbonic ethers, and also the acidylalkylthiosulphocarbamic ethers, $R''CO>N.CS.SR'$.—*Bull. Soc. Chim.*, xxix., No. 1.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 20, May 18, 1903.

Preparation and Properties of Cæsium-ammonium and Rubidium-ammonium.—Henri Moissan.—During his research on certain new compounds of cæsium and rubidium, the author prepares the compounds cæsium-ammonium and rubidium-ammonium, analyses them, and examines their properties. To obtain these compounds, liquid ammonia is brought in contact with the metal, the operation taking place in a current of dry carbon dioxide. The author utilises solutions of these compounds in liquid ammonia for the preparation of the carbides of cæsium and rubidium, and also of the corresponding acetylenic acetylides of these metals.

Theory of Colour Indicators.—P. Vaillant.—An indicator can be defined as a weak acid or base whose molecule, RH or ROH, has a different colour to that of the ion R. This, the author thinks, is not correct, because there is no mention of the colour of salts of the indicator; these latter being, in fact, the only bodies which take part in the reaction. He would alter the definition to the following:—An indicator is a weak acid or base whose colour differs from that of its salts. He performs several experiments to uphold this definition.

Electrolysis of Alkaline Earth Sulphides.—André Brochet and Georges Ranson.—For the electrolysis of the alkaline earth sulphides, platinum, iron, or nickel can be used as anodes. Carbon will also serve, but if for some reason the reaction becomes oxidising, the oxygen complicates matters by attacking the electrode. The addition of sodium chloride does not modify the general course of the reaction, but under these conditions iron or nickel behave as soluble anodes. Baryta being without action on the polysulphides, the authors examine whether the electrolysis of barium sulphide without a diaphragm could constitute a method of preparation of this base diminishing or suppressing the reduction of the polysulphides. The increase in density of the cathode current is of no interest, the effect being barely sensible.

Action of Ethyloxalyle on Mixed Organo-magnesium Compounds.—V. Grignard.—When an organo-magnesium compound acts on ethyloxalyle, an unexpected secondary reaction takes place. The first phase is normal, and represented by the equation—

$$\begin{matrix} CO_2C_2H_5 \\ | \\ COCl \end{matrix} + 2CH_3MgI = \begin{matrix} CO_2C_2H_5 \\ | \\ C(CH_3)_2OMgI \end{matrix} + MgICl;$$

then the ethyloxalyle, which is present in excess, reacts on this compound as an acid chloride, etherifying the alcohol function in the following manner:—

$$\begin{matrix} CO_2C_2H_5 \\ | \\ C(CH_3)_2OMgI \end{matrix} + ClCO\cdot CO_2C_2H_5 = \begin{matrix} CO_2C_2H_5 \\ | \\ C(CH_3)_2O.CO.CO_2C_2H_5 \end{matrix} + MgICl,$$

i.e., a mixed oxalate of ethyl and of the glycolic ether, is formed.

New Method of Estimation of the Halogen Bodies in Organic Compounds.—H. Baubigny and J. Chavanne.—The authors' method for the estimation of halogen bodies in organic compounds is based on the use of an alkaline solution of bichromate in concentrated sulphuric acid. This mixture, when hot, energetically attacks organic matters, and if they contain chlorine or bromine these bodies are liberated in the free state, even in the presence of a silver salt, whilst iodine is oxidised and retained in the solution in the form of iodic acid. By this means the iodine is separated from the chlorine and bromine in a rapid manner.

Action of Alkaline Earth Bases on Alkaline Earth Salts of Pyrogallol-sulphonic Acids.—Marcel Delage.—The author describes the six substances which are prepared by the reaction of an alkaline earth base on a sulphonate of the same metal. These mixed compounds, containing in their molecule two different alkaline earth metals, are prepared under the same conditions as the homogeneous compounds.

New Method of Estimating Glycerin.—A. Buisine.—When potassium hydrate mixed with potash-lime acts upon glycerin at about 350°, the potassium acetate produced during the rise of temperature is decomposed in its turn nto methane and potassium carbonate. Therefore, at 350°, ithe reaction of potash lime on glycerin can be expressed by the equation $C_3H_8O_3+4(KOH)=2(CO_3K_2)+6H+CH_4$. Under these conditions, 725 c.m. of hydrogen and 242 c.m. of methane at 0° and 760° are obtained from 1 grm. of glycerin. This reaction can be applied to the estimation of glycerin by the measurement of the gaseous volume obtained.

MISCELLANEOUS.

The Metric System.—The Decimal Association, of Botolph House, Eastcheap, have published a pamphlet setting forth their reasons why the metric weights and measures should be made compulsory throughout the British Empire. They point out that at present we make difficulties for ourselves in relation to our foreign trade with metric countries, and lose business because we do not manufacture and sell in terms of the metric system. Another very good and powerful reason for the change is, we think, the relief that would be experienced by getting rid of our present confusing and complicated system of weights and measures, which are really familiar to very few people besides school-teachers; months, or even years, of our childhood are wasted in learning them, and in after-life most people have to refer to the "table-book." The period of transition from our old weights and measures to those of the metric system must necessarily be attended with some inconvenience, but the general feeling of the Chambers of Commerce, of the leading School Boards, and many other public bodies throughout the country is in favour of a short shrift of not more than two years, after which the new system should be compulsory.

The Aromatic Polycarbylamines.—Felix Kaufler.—The polycarbylamines are obtained by the action of potash and chloroform on the diamines, under well determined conditions, which are:—For 15 grms. of diamine, 100 grms. of potash dissolved in 200 c.c. of water, 40 c.c. of alcohol, 300 grms. of chloroform, and boiling for from two to five hours. *Paraphenylenedicarbylamine* crystallises in white rhombic tablets, becoming black at 40°, soluble in ether and benzene; it combines with bromine, giving a tetrabromide fusible at 137—138°. The *p*-phenylenedicarbylamine heated to about 230—250°, is transposed into the terephthalic nitrile, fusible at 222—223°. *Metaphenylenedicarbylamine* forms needles which become coloured when exposed to the air; they fuse at about 90° with decomposition, being transformed into the isophthalic nitrile, fusible at 154—155°. The 1.3.5-trimethyl-2.4-diamidobenzene, treated with chloroform and potash, gives a small quantity of hygroscopic needles which have been transformed into the corresponding nitrile; this latter fuses at 139—140°, and is the 1.3.5-trimethyl-2.4-cyanobenzene already known. The 2.4.6-triamidotoluene, treated under the same conditions, seems also to give a polycarbylamine; triamidomesitylene gives a compound fusible at 160°, which is the 1.3.5-trimethyl-2-oxy-4.6-diisocyanobenzene.—*Mon. f. Ch.*, vol. xxii., p. 1073.

Research on Lead and Manganese.—A. Trillat.—The tetramethyl base of diphenylmethane, $CH_2[C_6H_4N(CH_3)_2]_2$, in acetic solution, by reason of the formation of the corresponding hydrol, $CH.OH[C_6H_4N(CH_3)_2]_2$, gives a magnificent blue, stable at high temperatures with certain dioxides (lead, manganese, and copper). The application of this reaction, being very sensitive with the first two metals, can be applied as a means of detecting them.—*Comptes Rendus*, cxxxvi., No. 20.

MEETINGS FOR THE WEEK.

FRIDAY, 26th.—Physical (at the Physiological Laboratory, London University, South Kensington). Special General Meeting, 4 30. Science Meeting, 5. "Electrical Effects of Light upon Green Leaves," "Blaze-currents—(1) of a Vegetable Tissue, (2) of an Animal Tissue," and "Quantitative Estimation of Chloroform Vapour in Air by—(1) Oil Absorption, (2) Densimetry," by Dr. Waller. "The Temperature Limits of Nerve-action in Cold-blooded and in Warm-blooded Animals," by Dr. Alcock. "On the Movement of Unionised Bodies in Solution in an Electric Field" and "On the Passage of Nervous Impulses through the Central Nervous System," by Dr. Hardy.

Re Pirie *v.* The Company and Others.—The Electro-Chemical Co. (1900), Ltd., 1901, E. 85.—By orders of Mr. Justice Farwell.

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THE CHEMICAL NEWS.

Vol. LXXXVII., No. 2274.

ON THE THEORY OF REFRACTION IN GASES.*

By GEORGE W. WALKER, M.A., A.R.C.Sc.,
Fellow of Trinity College, Cambridge.

The present theories of refraction in gases lead to expressions for the refractive index, of which the formula—

$$\mu^2 - 1 = Nf(\rho)$$

may be taken as typical.

In the formula—

μ is the refractive index.
N is the number of molecules per unit volume.
ρ is the frequency of the waves.

and $f(\rho)$ is a function of ρ which depends on the assumptions made as to the constitution of the molecule.

The formula, although it explains the main features in the visible spectrum, cannot always be made to explain the measured temperature effects, even when allowance is made for the deviations from the gaseous laws of Boyle and Charles.

Again, in the case of the dielectric constant for some gases such as SO_2 and NH_3, the value of $K-1$ is much greater than the value of $\mu^2 - 1$.

In such cases we find that $\mu^2 - 1$ varies nearly as N, while $K-1$ is more nearly proportional to N/θ, where θ is the absolute temperature.

The theories are thus inadequate, and a modification is required which will give a greater dependence on temperature.

In the theories of Voigt and Lorentz the molecule is regarded as an aggregate of electrical doublets. The individual parts are assumed to have free periods of vibration, which are naturally identified with the spectral lines of the gas, and, therefore, must have a frequency independent of temperature.

The view adopted in the present paper is that, instead of free vibrations, we have constrained motion. Regarded from Prof. J. J. Thomson's point of view, the atom consists of a large positive particle and a large number of small negative ones. Instead of supposing that these negative particles can vibrate radially, I regard them as rolling on the surface of the positive one in constrained motion. The effective control on transmitted waves is thus the rotational energy of motion of the particles, and it must be proportional to the absolute temperature.

When, by collisions or otherwise the rotational motion becomes so great that the electric attraction is overcome by the centrifugal force, ionisation occurs. The frequency or frequencies of rotation at which this occurs are determined by the electrical attractions and are independent of temperature, although, of course, the higher the temperature the greater will be the amount of ionisation. I regard these frequencies as corresponding to the spectral lines, and it will be seen that the view explains the ionisation produced by ultra-violet light, and also agrees with the fact that luminosity is probably always connected with ionisation, *e.g.*, the characteristic lines come out in the electrical discharge through the gas.

Regarded simply as obstacles, the molecules must contribute a term to $\mu^2 - 1$, which is proportional to N and practically independent of the frequency.

The final formula obtained is—

$$\mu^2 - 1 = k_1 N + \frac{k_2 N}{\theta} f(\rho, \theta),$$

where k_1 and k_2 are constants and $f(\rho, \theta)$ is a function of ρ and θ. The function is fully discussed in the paper.

The formula is shown to be capable of accounting for all the known facts connected with the dielectric constant and the refractive index, while the absorption of ultra-violet light and apparent absorption, due to selective reflexion in the infra-red, is also explained

Notwithstanding the very complex and varied facts in air, hydrogen, carbon dioxide, ammonia, and sulphur dioxide, complete numerical agreement between the measurements of $K-1$ and $\mu^2 - 1$ as regards both absolute magnitude and dependence on pressure, temperature, and frequency, has been established.

* Abstract of a Paper read before the Royal Society, May 28th, 1903.

THE HYDROLYSIS OF FATS *IN VITRO* BY MEANS OF STEAPSIN.*

By Dr. J. LEWKOWITSCH
and
Dr. J. J. R. MACLEOD, Mackinnon Scholar.

A few months ago, one of us (J. L.) stated (*Journ. Chem. Soc. Ind.*, 1903, p. 67) that he had made a series of experiments in which lipase was allowed to act on cotton-seed oil, and that he had only been able to obtain hydrolysis amounting to 3 per cent. Dr. Macleod then suggested that it would be of considerable interest to ascertain the extent to which steapsin could carry the hydrolysis under the same conditions. We therefore decided to investigate this question conjointly, and we are now in a position to show beyond doubt that steapsin is capable of hydrolysing (saponifying) fats outside the organism to a very great extent. As this fact appears to us of considerable physiological importance, inasmuch as the quantitative experiments have hitherto been made almost entirely on monobutyrin and simple esters,† we publish this preliminary notice without referring to the literature *in extenso*. This will be done after the completion of the experiments we have in hand.

Preparation of the Steapsin Solution.

The steapsin solutions A and B (see table) were prepared from fresh ox pancreas. The pancreas was freed of fat, minced, and 200 grms. ground up in a mortar with water. In the case of preparation A, 0·1 per cent of mercuric chloride was added, and in B some thymol. The preparations were then digested in the incubator at body temperature for twenty hours.‡ Next they were filtered, and the filtrate examined for steapsin by vigorously shaking 2—3 c.c. in a test-tube with a few drops of filtered butter-fat, adding a drop of an alcoholic solution of phenolphthalein, and then decinormal caustic soda solution, till a deep red colour was obtained. Exactly the same mixture was placed into a second test-tube, the pancreatic extract having, in this case, been heated to destroy its ferments. The preparations were incubated at 37° C. After about half-an-hour the preparations were examined. In the case of the steatolytically active mixture, the contents of the test-tube were found to be discolourised, and the amount of decinormal caustic soda solution necessary to restore the original red tint was ascertained. Preparations C and D were obtained from

* A Paper read before the Royal Society, May 28th, 1903.

† Nencki ("Spaltunge der Säureester der Fettreihe und der Aromatischen Verbindungen im Organismus und durch das Pancreas," *Arch. fur Exper. Path. u. Pharmak*, vol. xx., p. 367) tested the action of an aqueous extract of pancreas on mutton fat, but found hydrolysis to proceed only to about 20 per cent. By adding bile to the digest the saponification amounted to about 60 per cent. Pawlow ("The Work of the Digestive Glands," translated by W. H. Thompson, London, 1902) also records determinations by Dr. Walther (pp. 29, 39) of the steatolytic action of pancreatic juice obtained from a fistula, but the results do not give us an estimate of the actual amount of hydrolysis effected. They were used by the workers for comparative observations.

‡ These are the methods recommended by Ferd. Klug ("Ueber Gasentwickelung bei Pankreasverdauung, *Pflüger's Archiv*, 1898, vol. lxx., p. 329).

200 grms. minced fresh pig pancreas by simply triturating in a mortar with twice the bulk of water. In these cases the preparations were not incubated, for it was evident that in the previous experiments with A and B the steapsin had been destroyed, as the preparations, before incubation, were very active steatolytically when tested by the above method, but only very slightly so after incubation; probably this was due to the action of trypsin on steapsin. It was also noticed in preparations A and B that the steapsin remained on the filter-paper when the solutions were filtered, the filtrates having much weaker steatolytic powers than the precipitates. Preparations C and D were, therefore, only filtered through muslin.

Preparation of the Emulsion of Fat and Steapsin.

One hundred grms. of cotton-seed oil, or lard, were weighed out and carefully triturated in a mortar with measured quantities of the pancreatic extract. Great care was taken to obtain a complete emulsion. The emulsion was then poured into bottles which were well corked to exclude growth of fungi, and allowed to stand at the ordinary temperature.* If the temperature was raised too rapidly, say by immersion in a water-bath kept at 30° or 35° C., the emulsified mass would separate into two layers, and no hydrolysis would then take place. It is therefore of the greatest importance to carefully observe the mixture for some hours, and to thoroughly shake them up as soon as signs of separation are noticed, in order to restore the state of emulsion. A good plan is to immerse the well-shaken emulsion in cold water, or to let it stand in the open during the night. After a few days, distinct hydrolysis is noticeable. In the case of cotton-seed oil, the outward sign of hydrolysis is the hardening of the mass, due to the fatty acids that have been formed.

Consideration of Results.

The accompanying table contains a series of observations made on cotton-seed oil and lard. The amount of hydrolysis was measured by the percentage of free fatty acids, expressed in terms of oleic acid. The experiments with A, B, and C were started on February 19th, and those with D on March 5th. The first observations were made after a lapse of four days. The delay was caused through some of the emulsions having separated into two layers, which necessitated the re-establishing of the state of emulsion by frequent shaking. It will be noticed that in those experiments with cotton-seed oil, in which neither acid nor alkali had been added, hydrolysis had reached after four days, in the case of preparation C, from 22·9 per cent (No. 5) to 32·8 per cent (No. 6), and in the case of preparation D, from 31 per cent (No. 11) to 37·1 per cent (No. 9). After another seven days, samples Nos. 11 and 9 had reached 46·3 per cent and 44·3 per cent respectively. As it was not expected that further hydrolysis would proceed very rapidly, some time was allowed to elapse before the next tests were taken. It will be seen from the table that the highest percentages of hydrolysis, when neither acid nor alkali was added, were 86·7 per cent in the case of preparation C (No. 6), and 83·8 per cent in the case of preparation D (No. 10). In both cases the steapsin had been allowed to act for fifty-six days. Whereas the experiments made with C show that the amount of hydrolysis increases with the amount of steapsin mixed with the oil, no such striking regularity is apparent in the case of preparations D (Nos. 9 to 11).

Further experiments were made with cotton-seed oil under the same conditions, only with that difference that either dilute acid or dilute caustic soda was added. So far, no decisive influence of either acid or alkali has been noticed, and from the experiments recorded here, no definite conclusions can be drawn.

Curiously enough, the hydrolysis of lard proceeds at a very much slower rate, reaching only about one-third of

No.	Preparation.	Cubic centimetres of preparation per 100 grms. of cotton-seed oil or lard.	Date on which started.	Added to emulsion.			Percentage of free fatty acids formed.					
				Acid.	Alkali.		Feb. 23.	March 2.	March 9.	March 16.	April 16.	May 1.
		Cotton-seed Oil.										
1.	A 1	10	19/2/03	0	0	—	—	0·95	Separation into two layers had taken place.			
2.	A 2	20	19/2/03	0	0	—	—	0·8	"	"	"	
3.	A 3	16	19/2/03	0·5 c.c. of 2 per cent acetic acid	0·5 c.c. 1/10 normal NaOH	—	—	1·14	"	"	"	
4.	B	10	19/2/03	0	0	—	—	0·95	"	"	"	
5.	C 1	20	19/2/03	0	0	—	22·9	43·3	48·4	80·6	"	—
6.	C 2	30	19/2/03	0	0	—	32·8	49·9	60·45	86·7	—	—
7.	C 3	25	19/2/03	0·5 c.c. of 2 per cent acetic acid	0·5 c.c. 1/10 normal NaOH	—	10·22	26·4	41·04	48·8	74·7	—
8.	C 4	30	19/2/03	0	0	—	31·25	39·5	55·4	63·1	—	—
9.	D 1	30	5/3/03	0	0	—	—	—	37·1	44·3	68·3	70·2
10.	D 2	50	5/3/03	0	0	—	—	—	32·7	46·4	71·5	83·8
11.	D 3	60	5/3/03	0	0	—	—	—	31·03	46·3	60·8	79·5
12.	D 4	60	5/3/03	0·5 c.c. of 2 per cent acetic acid	0·5 c.c. 1/10 normal NaOH	—	—	—	30·4	45·2	65·3	73·7
13.	D 5	60	5/3/03	0	0	—	—	—	36·5	44·9	66·4	73·5
14.	D 6	30	5/3/03	0	0	—	—	—	31·4	43·8	74·1	74·3
15.	D 7	50	5/3/03	1 c.c. of 2 per cent acetic acid..	1 c.c. 1/10 normal NaOH..	—	—	—	37·66	44·5	65·2	77·2
		Lard.										
16.	D 8	50	5/3/03	0	0·5 c.c. 1/10 normal NaOH	—	—	—	8·98	9·2	29·9	46·7
17.	D 9	80	5/3/03	0	1 c.c. 1/10 normal NaOH..	—	—	—	12·2	14·4	20·7	22·9

* Most of the preparations kept free from infection during the time these experiments lasted. Only a few became covered with growth of *Penicillium glaucum* after the lapse of about four weeks.

the hydrolysis noticed in the case of cotton-seed oil. Since the consistency of lard favours the state of emulsion, one would have expected the opposite result. The last two experiments with lard seem to show that an increased amount of caustic soda, whilst favouring hydrolysis at the commencement, seems later on to retard the action of the steapsin, notwithstanding the larger amount of the latter.

The numbers recorded in the table show that the steapsin is not capable of producing the reversible reaction which it was thought, reasoning by analogy, this enzyme might produce.

These preliminary experiments are very interesting from a physiological point of view; they proved for the first time that it can be demonstrated by the usual quantitative methods of fat analysis that steapsin is a very powerful fat-splitting ferment.

We are now investigating the action of steapsin and of lipase on fats, in the presence of bile, small quantities of soaps, and a number of other substances which suggest themselves from a physiological point of view.

ON THE OPTICAL ACTIVITY OF THE NUCLEIC ACID OF THE THYMUS GLAND.*

By ARTHUR GAMGEE, M.D., LL.D., F.R.S., Emeritus Professor of Physiology in the Owens College, Victoria University, and WALTER JONES, Ph.D., Associate Professor of Physiological Chemistry in the Johns Hopkins University.

We have lately shown the dextrorotatory character of the nucleoproteids of the pancreas, thymus, and suprarenal gland (Gamgee and Jones, "On the Nucleoproteids of the Pancreas, Thymus, and Suprarenal Gland, with especial reference to their Optical Activity," *Roy. Soc. Proc.*, 1903, vol. lxxi., p. 385). We have, in the course of our investigations, shown that the "nucleins" possess a stronger rotation than the "nucleoproteids," properly so-called, and from which they are derived, and in the researches which we have planned and which naturally are suggested by our previous work, the first step appeared to us to be to determine the optical activity of the nucleic acids corresponding to the nucleoproteids investigated by us.

In the present paper we shall confine our attention to the optical activity of thymus-nucleic acid, prepared by the method of Kossel and Neumann (*Ber.*, vol. xxvii., p. 2215). We adhered closely to the method recommended by these chemists, which furnishes with great ease a colourless product, yielding colourless and perfectly transparent solutions admirably adapted for polarimetric observations. From 6 kilogrms. of trimmed thymus, Kossel and Neumann obtained 120 grms. of pure nucleic acid. From 600 grms. of the gland, we obtained 9·5 grms., though no special pains were taken to work even in an approximately quantitative manner. Our purified product, like that of Kossel and Neumann, was free from proteid and barium.

1. An amount of nucleic acid weighing 1·109 grms. was suspended in water and dissolved by the cautious addition of dilute solution of ammonia in small quantities, so that when solution had been effected the reaction of the solution towards litmus was neutral. The volume of the solution was made up to 100 c.c. and it was then examined polarimetrically.

Weight of substance (W)	1·109 grms.
Volume of solution (V)	100 c.c.
Length of tube (L)	200 m.m.
Observed angle (α)	+3° 29'.

$[\alpha]_D = +156{\cdot}9°$.

2. Ten c.c. of the above neutral solution were diluted with 10 c.c. of distilled water, and the resulting solution was examined polarimetrically.

W = 1·109 grms.; V = 200 c.c; L = 200 m.m.; $\alpha = 1° 43'$.
$[\alpha]_D = +154{\cdot}2°$.

3. Ten c.c. of the solution used in the last experiment were further diluted with 10 c.c. of distilled water and the resulting solution was examined.

W = 1·109 grms.; V = 400 c.c.; L = 200 m.m.; $\alpha = +0° 52'$.
$[\alpha]_D = +156{\cdot}4°$.

The above observations indicate that solutions of the nucleic acid of the thymus are powerfully dextro-rotatory, but that the specific rotation of neutral solutions does not vary appreciably with dilution, the variations in the results of the three sets of observations recorded above falling within the probable limits of error. Similar results had already been obtained with solutions of the nucleoproteid of the pancreas, although the limits of dilution in that case were not so great as in the present instance.

On the Influence of the Reaction of the Solution on the Optical Activity of the Nucleic Acid of the Thymus Gland.

The observations about to be referred to indicate a very remarkable influence exerted by the reaction of the solution on the optical activity of the nucleic acid under discussion. The rotation is notably influenced by the acidity of the solution; it reaches a maximum at a certain degree of acidity and then decreases. On the other hand, the addition of ammonia in sufficient proportion will render a solution of thymus-nucleic acid optically inactive, though neutralisation of the acid will restore its pristine activity. It is to be noted, however, that there is no abrupt change around the neutral point, a statement which is illustrated by the fact that two solutions of equal concentration may be prepared which are indistinguishable in so far as their optical rotation is concerned, one of which is faintly, though distinctly, acid to litmus, while the other is alkaline.

4. Twenty-five c.c. of the original neutral solution of nucleic acid employed in the first set of experiments were made decidedly acid by the addition of a trace of 20 per cent acetic acid. The change of volume was so small as to be negligible. The solution was then subjected to polarimetric examination, with the following results:—

W = 1·109 grms.; V = 100 c.c.; L = 200 m.m.; $\alpha = +3° 30'$.
$[\alpha]_D = +157{\cdot}8°$.

5. Twenty-five c.c. of the original solution were correspondingly made distinctly alkaline with ammonia and polarimetrically examined:—

W = 1·109 grms.; V = 100 c.c.; L = 200 m.m.; $\alpha = +3° 31'$.
$[\alpha]_D = +158{\cdot}7°$.

The two above sets of experiments show that determinations of the optical activity of thymus nucleic acid may be made in a neutral or quasi-neutral fluid, without fear of variation caused by inaccuracy in observing the point of exact neutrality. The following experiments, however, demonstrate that the rotation is markedly changed by the addition to a neutral solution of thymo-nucleic acid either of a considerable amount of acetic acid or of ammonia.

6. Twenty c.c. of the original solution were treated with one-tenth of a c.c. of 20 per cent acetic acid and the solution was polarimetrically examined:—

W = 1·109 grms.; V = 100·5 c.c.; L = 200 m.m.; $\alpha = +3° 33'$.
$[\alpha]_D = +160{\cdot}4°$.

7. Ten c.c. of the solution used in 6 were treated with 0·3 c.c. of 20 per cent acetic acid and polarimetrically examined:—

W = 1·109 grms.; V = 101·5 c.c.; L = 200 m.m.; $\alpha = +3° 36'$.
$[\alpha]_D = +164{\cdot}7°$.

Up to this point we observe an increase in the specific rotation of the nucleic acid. If, however, as in the two

* A Paper read before the Royal Society, May 28th, 1903.

following experiments, the amount of acetic acid is increased the optical rotation undergoes diminution.

8. Ten c.c. of the original solution were treated with 1 c.c. of 20 per cent acetic acid and then polarimetrically examined:—

W = 1·109 grms.; V = 110 c.c.; L = 200 m.m.; $\alpha = +2°29'$. $[\alpha]_D = +123°$.

The remarkable influence of solution of ammonia is illustrated by the following observations:—

9. Twenty c.c. of the solution which had been used in observation 5 were treated with 0·5 c.c. of 10 per cent solution of ammonia and polarimetrically examined:—

W = 1·109 grms.; V = 102·5 c.c.; L = 200 m.m.; $\alpha = +2°40'$. $[\alpha]_D = +123·4°$.

10. The solution used in Experiment 9 was treated with an equal volume of 10 per cent ammonia and the resulting solution examined:—

W = 1·109 grms.; V = 205 c.c.; L = 200 m.m.; $\alpha = +0°35'$. $[\alpha]_D = +50·8°$.

11. The solution used in Experiment 10 was further diluted with an equal volume of 10 per cent ammonia, when the solution was found to be optically inactive.

Our observations have shown us, as has been mentioned at an earlier part of this paper, that the diminution or abolition of optical activity which is induced by alkalis in solutions of thymo-nucleic acid are not permanent, the addition of acid restoring the primitive optical condition.

Bülow ("Ueber aschefreies Eiweiss," *Pflüger's Archiv*, 1894, vol. lviii., p. 207) has shown that the optical rotation of proteids varies with changes in the reaction of their solutions, and Framm ("Untersuchungen über die specifische Drehung des β-Glutin," *Pflüger's Archiv.*, 1897, vol. lxviii., p. 144) studied especially the alteration brought about in the specific rotation of gelatin by the addition of acids or alkalis. The alterations observed by Framm, however, were probably due to fundamental chemical changes brought about by the acid or alkali on the proteid. This reasoning cannot, however, be applied to the case of the nucleic acid of the thymus gland, seeing that the addition of acid to an alkaline solution restores the optical activity.

At the suggestion of one of us (A. G.), Dr. Thomas B. Osborne has determined the optical activity of the nucleic acid which he separated from the wheat embryo, and to which he applied the name of triticc-nucleic acid (T. B. Osborne and I. F. Harris, "Die Nucleinsäure des Weizenembryos," *Zeit. f. Physiol. Chemie.*, September, 1902, vol. xxxvi., heft 2, p. 85). Dr. Osborne ("The Specific Rotation of the Nucleic Acid of the Wheat Embryo," *Amer. Journ. of Physiol*, April 1, 1903, vol. ix., No. 2, p. 69) has found that this nucleic acid is dextrorotatory, though the degree of rotation is considerably influenced by the concentration of the solution. A solution containing 4 per cent of tritico-nucleic acid possessed a specific rotation $[\alpha]_D = +73°$.

Estimation of the Methoxyl Groups in Sulphurised Compounds.—Felix Kaufler.—Zeisel's method does not give good results with sulphurised compounds; the author has modified it, and made it applicable to the derivatives in which the methoxyl group is easily saponifiable by alkalis. The weighed substance is placed in a small flask, and heated to boiling with a solution of caustic potash. The vapours pass through a U-tube containing anhydrous sulphate of copper heated to about 90°, which absorbs the water, but allows the alcohol to pass; this latter is collected in a Winkler absorbing apparatus containing hydriodic acid, and kept very cool. The whole apparatus is traversed by a slow current of air throughout the operation. When the saponification is terminated, the hydriodic solution is heated, and the iodide of methyl is collected in nitrate of silver as in Zeisel's method.—*Mon. f. Ch.*, vol. xxii., p. 1105.

ESTIMATION AND ORGANIC ANALYSIS OF VERY SMALL QUANTITIES OF GLYCERIN.

By MAURICE NICLOUX.

Estimation.—The general method I gave first for the estimation of small quantities of alcohol has already had a number of applications. A certain number of reducible or simply oxidisable organic bodies can be estimated, when they are in very small quantities, by means of bichromate of potash and sulphuric acid, thanks to the difference of tint—a true change from bluish green to yellowish green corresponding to the absence or presence of a very slight excess of bichromate in the bluish green solution of sulphate of sesquioxide of chromium. It is in this manner that glycerin,* methylic alcohol, formic aldehyde, and formic acid in the state of purity† bear witness to this method.

I will summarise the method of estimation in so far as glycerin is concerned, and it does not differ much from that for the estimation of alcohol.

A solution is prepared of 19 grms. of pure crystallised bichromate of potash per litre, and a burette graduated to 1/10th c.c. is filled with it. Five c.c. of the liquid in which the glycerin is to be estimated is measured off and placed in a test-tube. Pure sulphuric acid at 66° B. ($D_{15} = 1·842$) is added in considerable excess, 5 to 7 c.c. The solution becomes very hot. The bichromate is then added very gradually, taking care to shake well, and heat carefully to boiling between each addition of bichromate, and also just at the moment when the colour changes from bluish green to a persistent yellowish green. The volume of the bichromate is then noted.

If the solutions contain more than 1 part of glycerin per 1000, which is easily detected, as more than 2 c.c. of bichromate are necessary to obtain the persistent yellowish green colour, we dilute so as to bring the proportion of glycerin below 1 grm. per litre—proportions for which the difference of tints is more easily recognised.

I have said that the volume of bichromate which gives the yellowish-green colour must be noted. It represents almost exactly the proportion of glycerin present. Consequently, strictly speaking, 5 c.c. would suffice for the estimation. In any case, to make absolutely certain, and to confirm the preceding figure, it is necessary to finish in the following manner. Repeat two experiments:—First experiment: Take 5 c.c. of the solution, add the previous amount of bichromate, less 1/10th of a cubic centimetre, then the sulphuric acid. Heat to boiling for one minute. The tube ought to be a bluish-green. Second experiment: Take 5 c.c. of the solution, add the previous volume of bichromate, then the acid. Heat as before, and the tube ought to be a yellowish-green. If this the case, the estimation is finished and the original figure is correct. If not, as may sometimes happen, and the last tube is still a bluish-green, add 1/10th c.c. of bichromate and the change to yellowish-green will take place; the figure is then 1/10th c.c. higher. With practice we can bring the estimation with two different volumes of bichromate to within 1/20th c.c.

The calculation is then extremely simple. Let n be the number of cubic centimetres or fractions (comprised betweed 0 and 2) indicated by the burette to obtain the yellowish-green colour; the solution of bichromate at 19 grms. per litre, is calculated in such a manner that if we operate on 5 c.c., the tint limit being the yellowish-green, we get glycerin in grammes per cubic centimetre of solution $= n/2000$ (n expressed in c.c.).

* It was MM. Bordas and de Raczkowsky who had the idea of applying my method for the estimation of alcohol to the estimation of glycerin. But the calculation, otherwise correct, of a false equation of oxidation had the effect of preventing them from realising it. For further details and bibliography, consult M. Nicloux, "On the Estimation of Small Quantities of Glycerin" (*Bull Soc Chim*, 1897, Series 3, vol. xvii., p. 455; and *Comptes Rendus de la Soc. de Biol.*, 1897, Series 10, vol iv., p. 698).

† M. Nicloux, "Estimation of Small Quantities of Methylic Alcohol, Formic Aldehyde, and Formic Acid" (*Bull. Soc. Chim.*, 1897, Series 3, vol. xvii., p. 839).

For proportions of glycerin less than 0·5 grm. per litre, it is best to dilute the 19 grm. per litre solution of bichromate, and make one of 9·5 grm. per litre; the formula then becomes:—

Glycerin in grammes per cubic centimetre of solution = $n/4000$ (n, expressed in c.c.).

To beginners especially in this method of estimation I would advise the use of six pairs of control tubes, each pair for a different, but known dilution of glycerin in water, below 1 per 1000, being for a bluish-green and a yellowish-green tube. In this manner, besides an accurate estimation, we get the exact intensity of the yellowish-green colour chosen as the limit.

The relative inherent error of this method is about 5 per cent; it may go down to 2·5 per cent, and less, in experienced hands, but it will never rise above 10 per cent even on the first time of trying.

The absolute error is about 1/20th m.grm. for proportions between 1 grm. and 0·5 grm. of glycerin per litre, and 1/40th m.grm. for proportions less than 0·5 grm. per litre.

Organic Analysis.—If we take care to work with the given amount of pure sulphuric acid, not diluted, the reaction is always identical; it corresponds to the complete oxidation of the glycerin into carbonic acid and water; the quantity of bichromate used indicates the amount, and the measurement of the carbonic acid produced will give the confirmation.

For this purpose I have devised the following arrangement:—

A tube 75 c.m. long and 2·5 c.m. diameter, closed at the bottom, and the upper end of which has been enlarged and ground, is closed hermetically by means of a glass stopper also ground.* Both surfaces are smeared with vaseline before making the joint. At about 3 c.m. from the upper end an elbow tube is sealed in, to which is fitted a length of stout rubber tube closed with a pinchcock.

Into the long tube we introduce 10, 15, 20, or 30 c.c. of pure sulphuric acid, according to circumstances (about double the volume of the glycerin solution), then carefully, a test-tube containing the solution under examination, and an amount of bichromate corresponding to the complete oxidation of the glycerin. This amount has been determined already by the method described above.

The tube is exhausted by means of a pump. A water pump will do for this first operation as the small amount of air left does not matter. The stopcock is closed, and the tube is sloped several times so as to bring the different substances into contact with each other. The reaction is completed by immersion in an oil-bath at 140°. The whole of the gas is now extracted, this time by means of a mercury pump, and collected in a graduated tube (graduated to 1/20th c.c.); a reading before and after the introduction of a little potash gives the carbonic acid by difference.

The following is a summary of one of these operations (No. 4 in the following table):—

In a test-tube we place about 10 c.c. of a solution of glycerin at 1·075 grm. per litre, or say 10·75 c.c., and 4·6 c.c. of bichromate at 19 grms. per litre (a very small excess of 0.3 c.c.), and 20 c.c. of sulphuric acid in the large tube. Close up, and pump the air out as described above. After the reaction has been allowed to take place, immerse for six minutes in the oil-bath at 140°. Extract the gas:—

Volume	16·9
KOH	8·2
CO_2	8 7

Note the pressure (H = 751) and temperature (t = 23). The weight of the carbonic acid is—

$$8{\cdot}7 \times \frac{1}{1{\cdot}0844} \times \frac{751 - 20{\cdot}8}{760} \times 1{\cdot}9774 = 15{\cdot}3 \text{ m.grms.}$$

* For greater security we could arrange a small cup joint filled with water, forming a hydraulic joint.

Now, the reaction $C_3H_3O_3 + O_7 = 3CO_2 + 4H_2O$ shows that 92 parts of glycerin give 132 parts of carbonic acid. Consequently, we should have CO_2 corresponding to 10·75 grms.:—

$$10{\cdot}7 \times \frac{132}{92} = 10{\cdot}75 \times \frac{33}{23} = 15{\cdot}42 \text{ m.grms.}$$

The following is the table of the results of experiments conducted in an identical manner. They show the extreme accuracy of the method.

Amount of glycerin.	Oxygen consumed.	Carbonic acid produced.	
		Theory.	Found.
M.grms.	M.grms.	M.grms.	M.grms.
8·5	10·38	12·20	12·7
16·5	20·08	23·67	23·6
10·15	12·78	15·06	15·0
10·75	13·10	15·42	15·3
5·375	6·54	7·66	7·7

We see at once the interest attached to this determination. We have done a true organic analysis: determination of the oxygen consumed and of the carbonic acid produced, by means of a very simple, rapid method, and only using a few m.grms. of material in aqueous solution.

This method, which can be further extended to the analysis of other organic compounds, will enable us, as far as glycerin in particular is concerned, to effect its identification; if we have to deal, for example, with reducing liquids containing glycerin, we can also effect the estimation of this important substance in experiments in the domain of pure chemistry and physiology. I propose to deal with this in a future paper.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 6.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, June 10th, 1903.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 212 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 212 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month of May has been exceptionally heavy, the amount recorded being 4·38 inches; the average rainfall for May is 1·75 inches; thus we have had an excess of 2·63 inches, and this, added to the previous one of 1·72 inches, makes a total excess for the year of 4 35 inches, or 49·9 per cent on the thirty years' average.

Our bacteriological examinations of 359 samples taken during the last month have given the results recorded in the following table. Besides these samples we have ex-

amined 259 others from special wells, standpipes, &c., making a total of 618 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	231
New River, filtered (mean of 76 samples) ..	11
Thames, unfiltered (mean of 26 samples) ..	4625
Thames-derived water, from the clear-water wells of seven Thames-derived supplies (mean of 179 samples)	19
Ditto ditto .. .. highest	128
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 26 samples) ..	351
River Lea, from the East London Company's clear-water wells (mean of 26 samples) ..	26

Of the 281 daily samples taken from the filter-wells of the Metropolitan Water Companies, ten samples, or 3·5 per cent, were sterile. There were seven samples, or 2·4 per cent, containing more than 100 microbes, and of these only two samples contained more than 150 microbes per c.c. The seven excess samples contained an average of 124 microbes per c.c.; in April five excess samples contained an average of 122.

From this it is satisfactory to note that in spite of the sudden and exceptional rainfall during the month of May, the bacteriological quality of the London water remains substantially as good as during the previous month, proving that adequate care has been expended and a high efficiency attained in the results of the filtration.

The exceptional rainfall at this time of the year in the watersheds of the Thames and the Lea has necessarily caused an increased amount of vegetable humus matter to pass into solution, although no more than has occurred on previous occasions at other periods of the year.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

COORONGITE: A SOUTH AUSTRALIAN ELATERITE.*

By ALEX. C. CUMMING.

The name coorongite was given many years ago to a peculiar substance found as a thin superficial deposit on the soil in the Coorong district of South Australia. A small sample was recently sent to the Chemical Laboratory of the University of Melbourne, and has been examined by me, under Prof. Masson's direction, with results to be described in the sequel.

Previous Accounts.—Coorongite is briefly described by Krausé ("Mineralogy," p. 138), and by G. C. Morris (*Proc. Acad. Nat. Sci. Philadelphia*, 1877, 131), and references have been found elsewhere; but by far the best and fullest account of it that I have been able to find is contained in a paper by J. R. Jackson, published in the *Pharmaceutical Journal* of 1872 (pp. 763 and 785). From this paper it appears that coorongite had, since its discovery in 1865, excited a good deal of interest both in Australia and in England, and that the question of its true nature and probable origin had been the subject of considerable discussion. Very different views were expressed, some regarding the substance as a bituminous hydrocarbon mineral, others believing it to be of vegetable origin. These discussions of thirty years ago appear to have been forgotten, and within the last year attention has been directed afresh to the same questions, still unsettled, by newspaper accounts of quests for mineral oil in the district where coorongite occurs. Jackson's paper was not known to me till after I had done the work to be described. My results are, in the main, corroborative of those he records and quotes from other observers, but additional information has been gained as to the chemical nature of the material.

* Read before the Royal Society of Victoria, October 9th, 1902. From the *Proc. Roy. Soc. Victoria*, 1903, vol. xv., Part 2, p. 134.

Description of Coorongite.—My specimens were in sheets varying from one-tenth to 1 c.m. in thickness. The substance varied in colour on the surface from greyish-black to black, but was uniformly black internally. It was soft, flexible, and elastic, resembling caoutchouc; one surface, probably the upper, was hard, black, and sponge-like; it contained a considerable quantity of sand and some vegetable fibres; it burnt readily with a white flame, melting before the flame, and giving, especially when extinguished, a characteristic odour, quite distinct from that from hydrocarbon minerals, and suggestive of burning animal or vegetable fats. Jackson gives the following analysis of coorongite by Dr. A. J. Bernays:—

Moisture	0·4682
Carbon	64·73
Hydrogen	11·63
Ash	1·79
Fixed carbon	1·005
Oxygen and unestimated	20·3768
	100·0000

The substance is insoluble in water and alcohol, and only partially soluble in carbon bisulphide, ether, chloroform, turpentine, benzene, and toluene, giving bright yellow solutions. This confirms observations of G. Francis, quoted by Jackson. On evaporation of the solvent a soluble body of low melting-point is obtained, the coorongite being thus separated into this body and a friable insoluble residue.

Separation into two Constituents by Extraction with Carbon Bisulphide.—100 grms. were cut up into small pieces and subjected to successive extractions with carbon bisulphide in a Soxhlet's extractor. After the first extraction the residue, which was quite friable, was rubbed to powder before adding fresh solvent. The product of each extraction was separately examined after evaporating off the carbon bisulphide. The results are shown in the following table:—

	Time of extraction. Hours.	Weight of extract. Grms.
1st Extraction	7	20·80
2nd ,, ...	12	2·78
3rd ,, ...	16	0·16
4th ,, ...	18	0·05
	53	23 79

Thus the sample yielded nearly 24 per cent of the soluble constituent. As the residue was found to contain from 30 to 40 per cent of sand and other mineral matter, the soluble constituent formed about one-third, and the insoluble constituent about two-thirds of the organic material. The results of the later extractions show that separation was complete.

The Soluble Constituent.—This is a clear, yellow, translucent, wax-like solid. Softens enough to flow if kept at 35°, and is quite fluid at 42°. Heated in an oil-bath it decomposed above 225°, yielding a little black distillate and a tar-like solid residue.

It dissolves readily, and in all proportions, in benzene, ether, toluene, chloroform, and carbon bisulphide, and is insoluble in water, methyl alcohol, and ethyl alcohol.

The composition was obtained by combustion with cupric oxide in a current of oxygen. The results agree closely with the figures calculated for the formula $C_{10}H_{18}O$.

	I.	II.	III.	Mean.	Calculated for $C_{10}H_{18}O$.
Carbon	77·86	77·94	77·92	77·91	77·92
Hydrogen	11 97	11·87	11·93	11·92	11·69
Oxygen (by diff.)	10·17	10·19	10·15	10·17	10·39

As the molecular weight could not be got by vapour density measurement, recourse was had to the freezing-point method, using benzene as solvent. The benzene

used was specially purified, and had the freezing-point 5·33° cor. Ice and water were used for freezing, and five observations were made at each temperature. The constant K for the benzene was determined by experiment with naphthalene, which gave a value of 5390.

1·080 grm. of the substance dissolved in 30·0 grms. benzene lowered the freezing-point 0·080°.

Using the formula—

$$M = K \frac{S}{\Delta L}$$

where M = molecular weight, K = a constant (5390 in this case) Δ = the depression produced, and L = weight of solvent, these figures indicate a molecular weight of 2425. The formula $(C_{10}H_{18}O)_x$ requires a molecular weight of 154, or some multiple thereof; and it would therefore appear that the value of x in benzene solution is 16 (M = 2464), or, in other words, the soluble constituent of coorongite is $(C_{10}H_{18}O)_{16}$ in benzene solution.

It is well known, however, that organic oxygen derivatives of the alcohol and acid kind are given to association in benzene solution, though they have simple molecules in other solvents, and that the molecular weight of a substance in benzene solution is often twice as great as the normal.

Observations were therefore made on the boiling-point of an ether solution of the substance, using ether purified by distillation from sodium immediately before use.

The whole of the ether (about a litre) distilled at 34·2°, but the first and last portions were rejected.

The boiling-point was raised 0·100° by the addition of 1·370 grm. of the material to 24·1 grms. of the ether, which by the formula—

$$M = K \frac{S}{\Delta L}$$

where K for ether = 2100, S and Δ have values given above, and L = 23·9 (allowing for vapour, &c.), gives the approximate value 1204 for the molecular weight, which is, within the error of experiment, half the value obtained in benzene solution. In these experiments, Beckmann's freezing-point and boiling-point apparatus were used with thermometers divided into hundredths of one degree C., and capable of being read by eye to 0·002°.

The results obtained indicate that the soluble constituent of coorongite is $(C_{10}H_{18}O)_x$, and that $x = 8$ in ethereal solution and 16 in benzene solution; x may, of course, have other values under other conditions.

Only an incomplete examination of the chemical properties of this substance has been made as yet. It is unacted on by acids except strong H_2SO_4, which chars it.

It combines with bromine, forming a black, viscous, sticky, semi-solid, readily soluble in carbon bisulphide and ether, but which has not yet been investigated.

It oxidises readily, as will be shown later. Attempts to saponify it led to negative results, though it is stated by Jackson to be saponifiable.

The Insoluble Constituent.—This was rubbed to a coarse powder during the extraction, and resembled brown cork filings mixed with much sand. Practically all the elasticity is lost during the carbon bisulphide extraction; it is combustible, burning with a white luminous flame, and melting before the flame; when burning it gives the same odour, like that of a burning fat, which coorongite itself gives. Analysis by combustion gave the following results for the organic matter:—

	I.	II.	Mean.	Calculated for $C_{10}H_{20}O_3$.
Carbon	64·16	64·28	64·22	63·83
Hydrogen	10·54	10·50	10·52	10·64
Oxygen (by diff.) ..	25·30	25·22	25·26	25·53
	100·00	100·00	100·00	100·00

The amount of ash (principally sand) varied from 30 to 40 per cent. The figures for the organic part agree remarkably well with those calculated for $C_{10}H_{20}O_3$, seeing that the material has undergone no purification other than the treatment with carbon bisulphide. Its dark colour suggests that it contains traces of some more highly carbonaceous material, which would account for the slight discrepancy.

This constituent, unlike the soluble one, was found to be saponifiable by hot alcoholic caustic potash, a soluble soap being obtained which yielded an insoluble fatty body on treatment with acid. This action has not yet been further examined.

Intermediate Oxidation Products.—The similarity of the formulæ $C_{10}H_{18}O$ and $C_{10}H_{20}O_3$ suggest that the insoluble ingredient is derived from the soluble one by a natural change involving hydration and oxidation combined.

Observations made in the course of the examination tended to confirm this, and to show that changes of this nature are readily brought about. In the following table are given the results of the combustions of three products obtained from portions of the soluble extract. No I. was got by blowing air through the carbon bisulphide solution; No. II. was formed during an attempt to extract some of the substance with methyl alcohol; No. III. was obtained when trying to distil it in steam. They were separated as completely as possible from unaltered substances by centrifuging the mixture at a temperature high enough to keep the latter in a molten condition. These three substances had the appearance of the clear first constituent of the coorongite, but containing an opaque, yellowish, granular precipitate. They could not be separated by solubility in carbon bisulphide or ether, but a partial separation was effected by centrifuging.

For comparison, the mean results of the combustions of the soluble and insoluble constituents and the calculated values are again given. It is evident from the table that products I., II., and III. are incompletely oxidised mixtures.

	C.	H.	O (by diff.).
Calculated for $C_{10}H_{18}O$ ..	77·92	11·69	10 39
Soluble constituent	77·91	11·92	10·17
Product No. II.	71·87	11·11	17·02
Product No. I.	70·35	11·42	18·23
Product No. III.	66·46	10·71	22·83
Insoluble constituent ..	64·22	10·52	25·26
Calculated for $C_{10}H_{20}O_3$ ..	63·83	10·64	25·53

The Ash.—The ash comprised about 25 per cent of the sample on which this work was done, but in a later specimen, since obtained from R. H. Walcott, Esq., F.G.S., of the National Museum, only 5·4 per cent of ash was found. The analysis failed to show the presence of any phosphates, which would be expected if the coorongite were of animal origin. The ash had the following composition:—

Silica	95·12
Aluminium and iron oxides	3·66
Calcium oxide	1·17
Sodium chloride	trace
	99·95

Mr. D. J. Mahony kindly examined the mineral part of coorongite, and found a number of species of typical freshwater diatoms. Only a small part consisted of diatoms, the ash being mostly sand, and it is doubtful whether the occurrence of these diatoms is more than accidental.

Conclusions.—Coorongite has been shown to consist of two substances: one with the formula $(C_{10}H_{18}O)_8$, and the other $(C_{10}H_{20}O_3)y$. The physical properties of the substance have earned it the name of Mineral Caoutchouc, and these formulæ favour the idea that it is really related to caoutchouc, which has the formula $(C_{10}H_{16})x$. Caoutchouc oxidises readily, even taking up oxygen from the air, and some of the substances connected with it and with gutta-percha have compositions and properties very similar to those of the two constituents of coorongite. The formulæ for these constituents are readily derivable from $C_{10}H_{16}$ by oxidation and hydration. However, for

the present the nature of coorongite must still be considered an open question, as much remains to be done in the further chemical investigation of its constituents.

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PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

Conversazione at Burlington House.

The Annual "Ladies' Night" at the Royal Society was held on Friday evening last, June 19th, and was attended by a numerous and distinguished company. The guests were received by the President, Sir William Huggins, O.M., &c., and Lady Huggins, and the members of the Council.

A certain number of the exhibits had been shown at the previous Soirée in May; among these were Sir Oliver Lodge's New Coherer for Wireless Telegraphy, Prof. Trouton's Meteorological Instruments, Drs. Anderson and Flett's Photographs and Specimens illustrating the late Eruptions in St. Vincent and Martinique, Sir William Crookes's "Spinthariscope," and experiments illustrative of some of the Properties of the Emanations from Radium, and these have been already dealt with in our columns.

Among the new exhibits we may mention that by Dr. O. J. Silberrad, on the Detonation of Small Shells; this comprised:—1. Common Lyddite shells illustrative of incomplete, and of successful detonation of Lyddite. 2. Armour-piercing Lyddite shells, showing complete detonation, and also the effect of supporting the shells in steel plates. 3. The obturator of a closed vessel which has been pierced by fragments of a tin case in which a high explosive was detonated; lent by the kindness of Sir Andrew Noble, F.R.S. 4. Photographs showing shell detonating, and also showing the destruction of a 15 pr. B.L. gun by the detonation of a 12 pr. Lyddite shell (charge, 1 lb. 9½ ozs. Lyddite).

Mr. F. Enock, F.L.S., showed some Colour Photographs of Living Insects to illustrate Protective Colouration and Resemblance. These were taken by the three-colour process from *living* insects.

Mr. Henry Crookes, F.C.S., exhibited a number of plate cultures and photographs illustrative of the Bactericidal Properties of the Emanations from Radium. Various cultures of bacteria were exposed to the action of 10 milligrms. of bromide of radium, through a mica screen, at about one inch distance from the surface of the plate. After having been subjected to the action of the radium emanations, "electrons" in these cases, the plates were incubated for twenty-four, forty-eight, or more hours. In every case it was found that the microbes were killed where they had been exposed to the radium, so that, on incubation, a bare space, free from bacterial growth, was left on the plate opposite the point where the radium had been placed. Among the bacteria experimented with were *B. liquefaciens*, *B. coli communis*, *B. prodigiosus*, &c.

The Rev. John M. Bacon's Aërial Photographs were very interesting. They were obtained recently from balloons under unique circumstances. They comprise pictures taken during the transit of the Irish Sea by sky from the Isle of Man to Dumfries, demonstrating the sea bottom at a depth of ten fathoms photographed from an altitude of 600 feet; views of London from aloft; cloud-land above the city, and other views.

Mr. Charles Baker showed a New Turbidimeter, for determining the Turbidity of Water. This instrument, designed by Mr. C. Anthony, jun., F.R.A.S., consists of two parallel tubes, one of which, of a standard length, closed at the ends by plates of glass, contains the water to be examined, and the other a Nicol prism. These two sources of light are examined through an eye-piece containing another Nicol prism, and by employing a rectangular prism between the eye-piece and the two tubes, the field of view is seen neatly dechroitomised, one half being illuminated by light coming through the tube containing the water under examination, whilst the other half receives light from the tube containing the Nicol prism. By rotating the eye-piece the illumination of the latter half of the field, seeing that the light has already passed through a Nicol prism, can be varied until it matches the half receiving the light through the standard thickness of water under examination. The amount of turbidity of the water can be read off to a rational scale, in which "I" represents perfect transparency, and "O" total obscuration.

The Marine Biological Association's exhibit always attracts attention; on this occasion it dealt with the Migration of Plaice in the North Sea; a new British species of the Polychæte family Sabellaridæ; and a number of living specimens of the Plymouth marine fauna.

The Condensation of the Radio-active Emanations of Radium and Thorium by Liquid Air was shown by Prof. E. Rutherford, F.R.S., and Mr. F. Soddy. The radio-active emanations of thorium and radium appear to be the residues of the thorium atom and radium atom respectively after the heavy positively charged particles, known as the "rays," have been projected. They have all the properties of inert gases of the argon family, and diffuse away from the radium and thorium compounds producing them. They can be condensed at the temperature of liquid air, and are again volatilised on raising the temperature. Their actual quantity is almost infinitesimally small, being quite invisible and unweighable, but their presence can be detected by their property of radio-activity.

Prof. Ernest Wilson exhibited the Cooper-Hewitt Mercury Vapour Lamp. The light, though almost entirely lacking in red rays, and therefore producing a considerable distortion in colour values, is for many purposes greatly superior to the ordinary electric light. The absence of red, well known as the colour most exciting and fatiguing to the eye, makes the light an almost ideal one for work where an absolute comparison of true colour values is not required. One of the greatest fields of application of the lamp is for all sorts of photographic purposes. The efficiency of the light is about ¼ watt per spherical candle-power, and under favourable circumstances as high as 0·3 watt per candle-power, being about seven times that of the ordinary electric glow lamp.

Two demonstrations with Lantern and other illustrations were given during the evening in the Meeting Room; the first by Prof. E. B. Poulton, F.R.S., on the discoveries of Mr. Guy A. K. Marshall upon the wet season and dry season forms of Rhodesian Butterflies; and the second by the Bioscope Company, who showed, among other interesting subjects, "living pictures" of battling with mountainous waves in Mid-Atlantic, Yellowstone Waterfalls, great tidal wave, "The Bore," sweeping up the Severn, and logging in Canada,

PHYSICAL SOCIETY.

Ordinary Meeting, June 12th, 1903.

Dr. R. T. Glazebrook, F.R.S., President, in the Chair.

Prof. S. P. Thompson showed Some Experiments on Shadows in an Astigmatic Beam of Light.

Two years ago Prof. Thompson showed before the Society some experiments on the shadows formed when a thin rod is placed in a beam of light which has passed through a tilted plano-convex lens. In those experiments the peculiar effects were chiefly due to the aberration known as coma. Following up his experiments, Prof. Thompson has investigated the shadows produced when a thin rod is placed in an astigmatic beam. The results are complicated by spherical or central aberration, which is generally present in the beam. The first experiments showed the effect of this aberration upon the shadow of a thin rod. A beam of light was passed through an ordinary convex lens and allowed to fall upon a semi-transparent screen. When the object was placed vertically so as to pass through the axis of the pencil anywhere between the foci formed by the central portion of the lens and the extreme zones, the shadow cast upon the screen was seen to be a vertical line passing through the centre of an oval. The oval is formed by the rod cutting out of the beam, the whole of the light from the zone of the lens which has its focus at the point upon the axis at which the rod is placed. The thickness of the rod determines the width of the zone and the consequent width of the oval shadow. Experiments were then shown, using an astigmatic beam with as little central aberration as possible. If the rod is placed at an angle of 45° to the vertical and passes through the axis of the pencil, then when it is either close to the lens or close to the screen the shadow makes an angle of 45° with the vertical also. As the wire moves from the screen to the lens the shadow turns over, 90° of the rotation taking place when passing from one focal line to the other. When the rod passes through the horizontal focal line, it cuts off the light from a thin vertical slice of the lens, and the shadow is therefore vertical. When it passes through the vertical line, the light is cut off from a horizontal slice of the lens, and the shadow is horizontal. When a thin rod inclined at 45° to the vertical is placed in a beam possessing both spherical and astigmatic aberrations, the shadow produced is a straight line when the rod is in contact with the lens or the screen. As the rod moves from one position to the other, the shadow turns over. It is also distorted in the process, so that its general shape is like the letter S. Prof. Thompson gave a simple formula for finding the inclination of the shadow of a rod when placed at any point on the axis of an astigmatic beam.

Prof. J. D. Everett expressed his interest in the subject. He said the experiments were very neat and the explanations clear. Assuming that the focal lines are at right angles, he indicated a simple method of determining the rotation of the shadow of a rod in an astigmatic beam. The formula arrived at was very similar to that given by Prof. Thompson.

Mr. Sowter said he was pleased to see Prof. Everett now agreeing with the assumptions which were embodied in his (Mr. Sowter's) paper on "Astigmatic Aberration," read before the Society last December. Prof. Everett had also verified some mathematical points brought out in that paper. It was unnecessary to prove that the section of the astigmatic beam was elliptical, for it has been known to be an ellipse in standard astigmatic pencils for the last fifty years. In the paper mentioned, it is shown that by reference to the elliptic sections any ray of the beam is defined by a constant eccentric angle, that the shadows or images on the picture screen are merely rotated or displaced in a pure beam, a rotation of 90° occurring between the focal lines, but that the shadows are distorted when spherical aberration is present in the lens system producing the beam.

A paper by Prof. F. T. Trouton and Mr. E. S. Andrews, "*On a Method of Determining the Viscosity of Pitch-like Solids*," was read by Prof. Trouton.

The various methods which have been proposed for measuring viscosity meet with difficulties when it is attempted to apply them for the measurement of the viscosity of bodies such as pitch. To obviate some of these difficulties a method has been devised in which a constant torque is applied to a cylinder of the substance, and the relative rate of rotation of the ends is observed. From these and the dimensions of the cylinder, the viscosity can be calculated by means of a formula deduced in the paper. The apparatus consists of a shaft turning freely on roller bearings with a pully attached, from which weights may be hung for the purpose of applying the constant torque. The shaft carries a square socket for the purpose of gripping the squared end of the cylinder of the substance used. The other end of the cylinder is held in a fixed socket, and the shaft and pulley carry a divided circle to enable the rate of rotation to be observed. The apparatus can easily be arranged for carrying out observations at different temperatures. Two new effects were at once observed:—(1) The coefficient of viscosity of bodies, such as pitch, is a function of the time; and (2) on removing the stress there is a flow back in the opposite direction which gradually diminishes to zero with time. These facts were illustrated by means of curves derived from experiments on a sample of "British pitch." On first applying the torque there is a rapid flow which gradually diminishes, and finally reaches a steady state. On removing the turning-couple the cylinder turns back some little distance, at first rapidly, then slowing down gradually to rest. In the initial stage a store of elastic energy is gradually accumulating which is preserved intact during the steady rotation, and given out on removal of the stress to produce the return flow. The rate of dissipation of the strain-energy stored in a cylinder of pitch when in a steady state of rotation, was determined by gradually removing the weights producing the torque at such a rate as to prohibit rotation in either direction. The fact that the strain energy disappears without any deformation occurring enables us to draw a distinct line between plastic and viscous substances. In a plastic substance, when held under deformation, the strain-energy does not lessen with time, while in a viscous substance it is dissipated. The apparatus was used for experiments on pitch, sodium stearate, and glass at high temperatures, and also to verify the formula employed.

Mr. Rollo Appleyard said that with materials such as Prof. Trouton had investigated, it was necessary to exercise great care in eliminating errors due to slip and other disturbances at the ends of the bars. For this reason it was, as a rule, better to attach the rotating-index pointer not to the clamp which applies the twist, but at a place at a little distance along the bar itself. A convenient way of doing this with these comparatively weak materials was to slip an indiarubber ring over the bar. Between this ring and the bar could then be held a piece of cork carrying a pointer. Instead of applying separate weights to a scale-pan in such tests, it led to smoother results if the weights were increased by the flow of water into a vessel. Mr. Appleyard thought that it was almost hopeless to seek for mechanical "constants" in respect to such highly extensible and complex substances as pitch, and suggested that for such materials, and perhaps for materials in general, it might be better to assume that the ratio of strain to stress is a function, possibly a logarithmic function, of the stress. The investigation of this function from small displacements right up to the breaking strain, would be more useful than figures based upon the assumed constancy of Young's modulus and Poisson's ratio.

Prof. Trouton, in reply to Mr. Appleyard, said that the rapid flow on first applying the torque was not due to any end effect, but was a property of the material. He also mentioned that he had determined the viscosity of shoe-

makers' wax by Stokes's method. A leaden bullet is allowed to fall through a tube filled with the wax, and from its rate of descent the viscosity can be calculated. The difficulty of following exactly the motion of the bullet can be overcome by using Röntgen rays. The results obtained from these experiments agreed very well with those obtained from the apparatus described in the paper.

A paper by Mr. O. W. RICHARDSON, on "*The Positive Ionisation produced by Hot Platinum in Air at Low Pressures*," was taken as read.

The experiments described in this paper were almost all made at temperatures so low that there was no appreciable negative ionisation. In examining the relation between the current from a positively charged hot platinum wire and the applied E.M.F. at low pressures, results were obtained which indicated that the value of the current fell off with time when the other conditions were kept constant. Further experiments showed that the current died away rapidly at first until it reached a steady value which only disappeared gradually. Calling this steady value of the current C_0, it is found that the value C at any time t is given by $C - C_0 = Ae^{-kt}$, where A and k are constants. It is shown that this is the form which would be obtained if the induced leak $C - C_0$ were produced by the monomolecular decomposition of some substance which gave rise to positive ions. The rest of the paper deals with the methods by which a wire which has lost the power of producing positive ionisation may have that power restored to it. It is shown that this can be done (1) by charging it negatively and allowing it to receive the positive ionisation from a fresh hot wire, (2) by exposing it to air for some time, and (3) by placing it in a vacuum-tube in which a luminous discharge is taking place. Experiments illustrating the nature, and determining the magnitude, of each of these effects are described.

THE TOKYO CHEMICAL SOCIETY.

THE Tokyo Chemical Society celebrated its Twenty-fifth Anniversary on May 9th, 1903, under the Presidency of Prof. JOJI SAKURAI, LL.D. There were present Baron D. Kikuchi, the Minister of Education; Baron H. Kato, the President of the Tokyo Academy of Sciences; Dr. K. Yamakawa and Dr. A. Hamao, the President and Ex-President of the Tokyo Imperial University; Prof. K. Mitsukuri, the President of the Zoological Society; Prof. N. Nagai, the President of the Pharmaceutical Society; Prof. F. Omori, the President of the Mathematical-Physical Society; Prof. K. Miura, the President of the Medical Society; and Prof. Oscar Loew, besides members and associates of the Society, numbering about seventy in all.

After the reports of the previous year by the retiring President, the Treasurer, and the International Atomic Weight Committee were presented and adopted, and two papers by Prof. M. Kuhara, of the Kyoto University, were read, the President gave an address on the history of the Society since its foundation in 1878, according to which the Society is making a very fair progress both in numerical strength and in the nature and quality of the papers communicated. Announcement was then made by the President that Robert William Atkinson, Esq., B.Sc., of Cardiff, Dr. Edward Divers, F.R.S., of London, Dr. Oscar Kellner, of Möckern, and Dr. Oscar Loew, of Tokyo, were elected to the Honorary Members of the Society. This was followed by an interesting paper by Prof. K. Ikeda on the development of chemical science in Japan, and by an elaborate paper by Prof. T. Takamatsu on the progress of chemistry in general within the last twenty-five years. Congratulatory addresses were then delivered by the Minister of Education and the President of the University, after which the members and the guests went over the exhibits of the objects of chemical interest, which were contributed by various chemical institutions in Tokyo.

In the evening the members and the guests sat together at dinner, again under the presidency of Prof. Joji Sakurai. After the health of the Emperor was most enthusiastically honoured, the PRESIDENT, in proposing the toast of the Honorary Members, spoke as follows in English:—

"Your Excellency and Gentlemen,—It is now my pleasant task to propose a toast, which has a peculiar importance, and which, I am sure, you will all drink with utmost enthusiasm. It is the toast of the Honorary Members of the Tokyo Chemical Society. The election to the Honorary Members of the Society, for the first time in the history of its existence, of four gentlemen—Mr. R. W. Atkinson, Dr. Edward Divers, Dr. Oscar Kellner, and Dr. Oscar Loew—distinguished alike for their scientific attainments and for the important parts they have played in the progress of chemistry in this country, has been, I assure you, one of the most pleasant functions in connection with the celebration of this jubilee. The names of these gentlemen are so familiar to us and their work so well known to the scientific world that any eulogy upon them would be perfectly superfluous, but I cannot let the occasion pass without expressing my deep-rooted conviction that, had it not been for their constant and untiring endeavour to encourage the study of science for its own sake, chemistry in this country would never have attained the position which it now holds. Although, gentlemen, Mr. Atkinson, Dr. Divers, and Dr. Kellner have already left us, it is my sincere hope that they may some day come back to our shores to see that the seeds they have planted are growing into trees and bearing fruit. At the same time, it is a source of intense pleasure to think that Dr. Loew is among us, ever active with the prosecution of research, and ever ready to lend his helping hands to those who would come to him for advice and counsel. I have now the pleasure of giving you, gentlemen, the toast of the Honorary Members, coupled with the name of Dr. Loew."

Dr. LOEW briefly replied in English.

The other toasts were "The Guests," proposed by Prof. Takamatsu, and replied to by the Minister of Education; "The Learned Societies," proposed by Prof. Matsui, and replied to by the President of the Tokyo Academy of Sciences; and "The Tokyo Chemical Society," proposed by Dr. Hamao, and replied to by the President.

NOTICES OF BOOKS.

Die Konstitution des Kamphers und seiner wichtigsten Derivate. ("The Constitution of Camphor and its most Important Derivatives"). By OSSIAN ASCHAN. Braunschweig: Friedrich Viewig und Sohn. 1903.

THIS book is a short monograph on the advances which have recently been made in our knowledge of the constitution of camphor and its derivatives. The concise and handy way in which the information is summarised will render the book useful, not only to those who devote themselves to the study of camphor, but also to all investigators of alicyclic compounds. The Bredt formula is adopted throughout the book as that which is most probably correct and least open to objections, though its claims to accuracy are not unfairly emphasised, an instance of the somewhat unusually unbiassed character of the monograph. A large portion of the book is devoted to the discussion and examination at considerable length of the different camphor formulæ which have been suggested, and the interesting manner in which this portion of the book is written is likely to give the reader an intelligent grasp of the difficulties to be overcome and the methods of attack to be adopted in dealing with problems of this class. If it does not make too great demands upon his time, the student can hardly follow any more in-

structive method of acquiring the power of making original investigations in the region of organic chemistry than that of studying the researches which have led up to the discovery of the constitutional formula of a substance such as camphor.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Edited by Franz Hofmeister. Band III. 9 and 10 Heft. Braunschweig: Friedrich Viewig und Sohn. 1903.

The history of the discovery of a hitherto unknown product of pancreatic auto-digestion is contained in this issue of these *Beiträge*. This substance, for which the name skatosine has been suggested from its apparently close relationship to skatole, was first isolated by Dr. Fritz Baum in 1899, and has since been subjected to further investigations at the Physiological-Chemical Institute at Strassburg. The results of these investigations are described, and additional information given in a paper by R. E. Swain. The formula of skatosine is $C_{10}H_{16}N_2O_2$, and it appears to stand in close relationship to the indol group of the albumen molecule, though it does not contain the indol residue as such. Among other papers of interest in this number are a preliminary communication describing still unfinished researches dealing with the proteolytic enzyme of yeast, and a short paper by Dr. Martin Jacoby on the question of the specific action of the intracellular ferments.

Berichte über Land- und Forstwirthschaft in Deutsch-Ostafrika. ("Reports on Agriculture and Forestry in German East Africa"). Band I. 3-5 Heft. Herausgegeben vom Kaiserlichen Gouvernement von Deutsch-Ostafrika. Heidelburg: Carl Winter's Universitäts Buchhandlung. 1903.

These three issues of the Government Reports of the Colonial Department of the Foreign Office on matters relating to agriculture and forestry are chiefly occupied with questions of biological interest. The reports have been carefully compiled, and the details to be found in them will no doubt be of use to those interested in these subjects. Statistics and descriptions are given as to the results of experiments in the cultivation of various crops in different parts of German East Africa, with, in some cases, reports on the analyses of the soils in various districts. Part 5 contains a short criticism of Dr. Wohltmann's essay on "The Prospects of Coffee Cultivation in the Mountains of Usambara," which was published in *Tropenpflanzer* in 1902, and in which, according to the author of this criticism, Dr. A. Zimmermann, the views expressed were more pessimistic than is warranted by facts.

CORRESPONDENCE.

THE RUSTING OF IRON.

To the Editor of the Chemical News.

Sir,—In an interesting paper by Prof. Dunstan recently transcribed into the Chemical News (vol. lxxxvii., p. 270) the causes of the rusting of iron are dealt with in some detail. Various facts are established or confirmed, and the composition of the rust is stated. In this last phase of the question Prof. Dunstan appears to have overlooked the fact that all ordinary rust contains ferrous iron and is magnetic. It follows that the formula which he suggests, $FeO_2(OH)_2$, cannot be accepted as general.—I am, &c.,

Bertram Blount.

76 & 78, York Street, Westminster, London, S.W., June 16, 1903.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 21, May 25, 1903.

Action of Acetylene on Cæsium-ammonium and Rubidium-ammonium. Preparation and Properties of the Acetylenic Acetylides, C_2Cs_2, C_2H_2—C_2Rb_2, C_2H_2, and the Carbides of Cæsium and Rubidium.—Henri Moissan.—Cæsium and rubidium form carbides of formula C_2R_2 and acetylenic acetylides, C_2R_2, C_2H_2, comparable with the same derivatives of the other alkaline metals. These new carbides decompose cold water, giving an alkali, with evolution of pure acetylene gas. They are in all respects similar to calcium carbide. They are very energetic reducing agents, combining in the cold with non-metals, with production of heat, and they easily decompose oxides below red heat. The acetylenic acetylides are explosive bodies, which, during the phenomena of reduction, cause violent reactions.

Combined Hydrogen contained in Reduced Copper.—Anatole Leduc.—This paper is in answer to a remark at the end of M. Armand Gautier's communication of January 5, 1903, on the subject of atmospheric hydrogen.

Decomposition of Lithium Carbonate by Heat.—P. Lebeau.—Under the action of heat lithium carbonate begins to decompose at about 600°, and even at this temperature the oxide has a vapour-tension which shows that it can be completely vaporised. A list of the vapour-tensions at temperatures varying from 580—1000° is given.

Electrolysis of Barium Sulphide with a Diaphragm.—André Brochet and Georges Ranson.—This research is a continuation of a previous one on the electrolysis of barium sulphide without a diaphragm. If a porous pot is used to separate the two poles, the primary reaction is the same; that is to say, sulphur—and, consequently, polysulphides—are obtained at the anode, barium—and, consequently, baryta and hydrogen—at the cathode. With a diaphragm there is no reduction of the polysulphides. On the other hand, the baryta which diffuses into the anode compartment being, under the conditions of the operation, without action on the very soluble polysulphides, can be separated and collected. The yield is practically the theoretical one.

Method of Decomposition of Mixed Organo-magnesium Compounds.—V. Grignard.—In the numerous synthetic reactions effected by means of mixed organo-magnesium compounds of formula R,MgX, it is always noticed that the compounds split in the same manner in the two monovalent groups, R and MgX. A single exception to this rule was noticed by M. Blaise, who found that, with ethylene oxide and C_2H_5MgBr, the reaction was

$$C_2H_5MgBr + \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \!\!>\!O = \begin{matrix} CH_2—C_2H_5 \\ | \\ CH_2—OMgBr \end{matrix}.$$

The author investigates this seeming exception, and succeeds in bringing this reaction in conformity with the general rule.

Acetones of Acetylenic Function. New Method of Synthesis of Pyrazols.—Ch. Moureu and M. Brachin.—The acetylenic acetones, $R—C\equiv C—CO—R'$, when reacting on the hydrazines give pyrazols. This new method of synthesis enables the authors to fix in a certain manner the constitution of pyrazols prepared with the non-symmetric β-diketones.

Certain Addition Products of Vinylacetic Acid.—R. Lespieau.—The isomerism of the crotonic and isocrotonic acids has been interpreted in two ways—(1) That isocrotonic acid is only vinylacetic acid, $CH_2=CH—CH_2—CO_2H$; and (2) that it is a stereo-

isomer of crotonic acid corresponding to the formula $CH_3—CH=CH—CO_2H$. The question as to the real constitution is still uncertain. The author investigates the question by obtaining the acids $CH_2Cl—CHCl—CH_2—CO_2H$ and $CH_2Br—CHBr—CH_2—CO_2H$.

Electrolytic Separation (1) of Manganese from Iron, (2) of Aluminium from Iron or Nickel, (3) of Zinc from Iron.—MM. Holland and Bertiaux.—The separation of manganese from iron can be effected electrolytically, the manganese being precipitated in the state of peroxide on the anode and the iron on the cathode. The authors overcome the practical difficulties connected with this separation. To separate iron from aluminium the metals must be in the form of sulphate to which ammonium citrate and SO_2 are added. When iron is separated from zinc electrolytically, the iron, by the addition of SO_2, passes into the form of ferrocyanide of potassium.

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Pentafluoride of Iodine.—Henri Moissan.

Synthesis of the Alkaline Hydrosulphites, and the Anhydrous Alkaline Earths.—Henri Moissan.

Preparation and Properties of Silicide of Vanadium.—Henri Moissan and A. Holt.

Preparation and Properties of a New Silicide of Vanadium.—Henri Moissan and A. Holt.—The above four papers have been noticed already in this column.

The Action of Carbonic Oxide on Dissolved Ferricyanide of Potassium.—J. A. Muller.—Already inserted in full.

Examination of the Action of Carbonic Oxide on Mangano-, Cobalti-, Chromi-, and Platinocyanide of Potassium.—J. A. Muller.—Already inserted in full.

Localisation of the Normal Arsenic in Animals and Plants; its Origins.—Armand Gautier.—The author has not yet been able to detect arsenic in fishes, either in the eggs or in the roe. In birds it is not found in the eggs, but it is found in the feathers; the coloured portion of the tail-feathers of a peacock contained as much as 0·25 m.grm. of arsenic in 12 grms. of the substance. Arsenic is also present in the down from the breast of a goose. Again, arsenic was always found, in variable proportions, in fresh and salt-water algæ, but is much more plentiful in the latter.

Action of the Alcohols on Chloroacetate of Methylene.—M. Descudé.—Chloroacetate of methylene dissolves in the alcohols, but not without decomposition. Slowly in the cold and very rapidly when heated, hydrochloric acid is formed, while at the same time a complex reaction takes place, and, if the product obtained is rectified, we have a mixture of acetic ether of formal corresponding to the alcohol used, and water; all the chlorine of the chloroacetate having been eliminated in the state of hydrochloric acid. With methylic and ethylic alcohols, the reaction is extremely energetic, but the separation of the resulting products is difficult. The same is not the case with the higher homologues, and this reaction then constitutes a convenient and advantageous method for the preparation of the formals, considering how easily the chloroacetate, which need not be pure for this purpose, can be prepared.

Sulphurised and Nitrated Compounds Derived from Sulphide of Carbon.—Marcel Delépine.—VIII. *Thiosulphocarbamic Ethers Derived from Ammonia*, NH_2CS_2R.—The action of the halogen ethers on thiosulphocarbamate of ammonium engenders the thiosulphocarbamic ethers or dithiourethanes non-substituted for nitrogen, $NH_2.CS_2.NH_4+RX=NH_2.CS_2.R+NH_4X$. The known ethers of this category were the ethylic and isopropylic ethers. The author shows that the successive action of a halogenised ether, then of an acidylised derivative, gives acidyldithiourethanes; it was thought, therefore, that if we could start with a body containing two radicals, a closed chain would be formed. This is done easily with the α-halogen ether salts. IX. *Imidothiocarbonic Ethers*, $NH=C(SR)(SR')$.—(Already noticed).

New Derivatives of Dichlorised Phthalic Acid.—E. C. Severin.—The author describes three new derivatives of phthalic acid. Dichlorised dialcoylamido *m*-oxybenzoylbenzoic acid,—

$$C_6H_2Cl_2<\begin{matrix}COC_6H_3<\begin{matrix}OH\\N(CH_3)_2\end{matrix}\\COOH\end{matrix},$$

is obtained by melting together 100 grms. of dimethylamidometaphenol with 160 grms. of dichlorised phthalic anhydride. After three hours the whole forms a hard mass of a deep violet colour, which is pulverised and boiled with a very small quantity of alcohol; this dissolves the products that have not entered into the reaction. After draining, it is washed with cold alcohol, and then dissolved in boiling alcohol; on cooling, small colourless crystals are deposited fusing at 191°. A small quantity of rhodamine is formed also. Dichlorised dimethylamido-*m*-oxybenzylbenzoic acid is obtained by reduction in acetic acid by means of hydrochloric acid and zinc. The reduced acid crystallises in small white crystals fusing at 195°. Dichlorised dimethyl-amido-*m*-oxyanthraquinone is obtained by direct condensation with concentrated sulphuric acid, heated for one hour on the water-bath. The solution is poured into cold water, the precipitate collected and dissolved in acetic acid. On cooling, small flakey crystals are obtained of a bronze-violet colour, fusing at 185°.

MISCELLANEOUS.

The Chemical Society.—An Extraordinary General Meeting will be held in the Society's Rooms on Thursday, July 2nd, 1903, at 6 p.m., to consider the proposal of the Council to make certain alterations in By-law I., and in Circulars Nos. 2, 3, and 4 in the Appendix. The proposed changes are:—

I. To alter By-law I., p. 13, lines 3 and 4, by deleting the words "one year." The By-law at present reads:—"and he shall be entitled, so long as his annual subscription be not one year in arrear, to one copy of the annual publications of the Society."

II. To alter the Circulars in the Appendix as follows:—In Appendix, No. 2, "Letter notifying the Election of a Member," 5th and 6th lines, p. 26, delete the words "the Assistant Secretary." After the words "before admission," add the words "Payment should be made direct to the Society's Bankers, either by Cheque or Post Office Order crossed a/c 'Chemical Society.' Your remittance should be accompanied by the enclosed Form with your Name and Address filled in." In Appendix, No. 3, "Annual Circular Letter of Treasurer," delete from "If paid" to end of circular, and substitute the same words as added in No. 2. In Appendix, No. 4, "Annual Circular Letter of the Treasurer to Fellows who are two years in arrear of their Subscriptions," delete from "Payments should be made" to end of circular, and substitute the same words as added in No. 2.

MEETINGS FOR THE WEEK.

TUESDAY, 30th.—Faraday Society, 8. "The Present Position of the Theory of Electrolysis," by W. C. Dampier Wetham, F.R.S. "Chlorine Smelting, with Electrolysis," by James Swinburne, M.Inst.C.E. "Total and Free Energy of the Lead Accumulator," by R. A. Lehfeldt, D.Sc. "Electrolytic Apparatus," by F. Mollwo Perkin, Ph.D.

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THE

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THE CHEMICAL NEWS.

VOLUME LXXXVIII.

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No. 2275.—JULY 3, 1903.

SOME PRELIMINARY OBSERVATIONS ON THE ASSIMILATION OF CARBON MONOXIDE BY GREEN PLANTS.*

By W. B. BOTTOMLEY,
Professor of Botany, King's College, London,
and
HERBERT JACKSON,
Assistant Professor of Chemistry, King's College, London.

During an investigation by one of us some years ago on "Carbon Monoxide in some of its Physiological Effects," a few experiments were made on plants, and it was noticed that a hyacinth, which had commenced growth and was showing a few small leaves, continued to grow for some weeks when placed in a bell-jar in which the air had been replaced by a mixture of 80 per cent of carbon monoxide and 20 per cent of oxygen. As this was contrary to the usually accepted ideas as to growth of green plants in carbon monoxide, a number of experiments were recently commenced with a view to determining how far carbon monoxide could replace carbon dioxide as a source of carbon supply for green plants. Although the hyacinth grew in carbon monoxide the experiment was not considered conclusive, because of the large stores of carbohydrates in the bulb. Young plants of *Tropæolum majus*, grown in sterilised sand and supplied with a nutritive solution free from all traces of carbonates, were therefore used. It was found that *Tropæolum* plants would not grow in air in which the carbon dioxide had been replaced by an equal quantity of carbon monoxide. When, however, the relative solubilities of the two oxides of carbon in water were taken into account, and the amount of carbon monoxide was increased proportionately—about twenty times as much carbon monoxide as carbon dioxide—the plants grew well, being healthy and normal. Experiments were also made with varying proportions of carbon monoxide in air free from all traces of carbon dioxide. The plants grew freely and well in proportions varying from 1 to 70 per cent of carbon monoxide, when care was taken that as the higher percentages of carbon monoxide were reached, oxygen was added so as to keep the amount of this gas approximately equal to that in normal air.

One very significant fact was noticed during the experiments. When in bright sunshine a negative pressure was always observed in the bell-jars containing plants growing in carbon monoxide. This result tends to confirm Baeyer's theory of photosynthesis. In normal photosynthesis the volume of oxygen given off is equal to the volume of carbon dioxide undergoing decomposition. If, however, carbon monoxide be used directly by the plant, only half the amount of oxygen would be given off, hence the negative pressure.

Experiments were also made to find if starch was formed in plants growing in carbon monoxide. *Tropæolum* plants growing in water culture solutions were placed in the dark for forty-eight hours, when the leaves were shown by the iodine test to be free from starch. Some of the plants were then placed in air free from carbon dioxide; others in carbon dioxide free air, but containing 10 per cent of carbon monoxide. All were then exposed to sunlight for three days, and again examined for starch. The plants grown in carbon dioxide free air had formed no starch, whilst those grown in carbon monoxide gave the iodine test most markedly. Sections of the green stems showed quantities of starch grains in the ground tissue, especially crowded around the vascular bundles, in the plants grown in carbon monoxide, but none in those grown in carbon free air.

Experiments on the germination and growth of seeds in carbon monoxide also gave satisfactory results. Seeds of *Lepidium sativum* were planted in sterilised sand, and placed in a mixture of 65 per cent carbon monoxide and 35 per cent oxygen. The seeds germinated, and formed healthy plants, growing quite normally for three weeks. Certain preliminary determinations of the amount of carbon in the seeds and in the plants point to the accumulation of organic carbon, and as the only possible source for this increase of carbon is the carbon monoxide, some of it must have been assimilated. These results are so important and the results so striking that it has been thought advisable to repeat the determinations with new and specially devised apparatus before quoting figures. Also it is intended to carry out further experiments with carbon monoxide, and with compounds in which the CO-group exists in combination.

In all these experiments with cabon monoxide, great care was taken that efficient absorbers of carbon dioxide were used, and the pressure in the bell-jars was regulated by potash-sealed valves.

The present communication is only a note to indicate the general bearings of the research, and does not give any account of many experiments and observations of interest which the authors hope to give later in a detailed paper.

* A Paper read before the Royal Society, June 18, 1903.

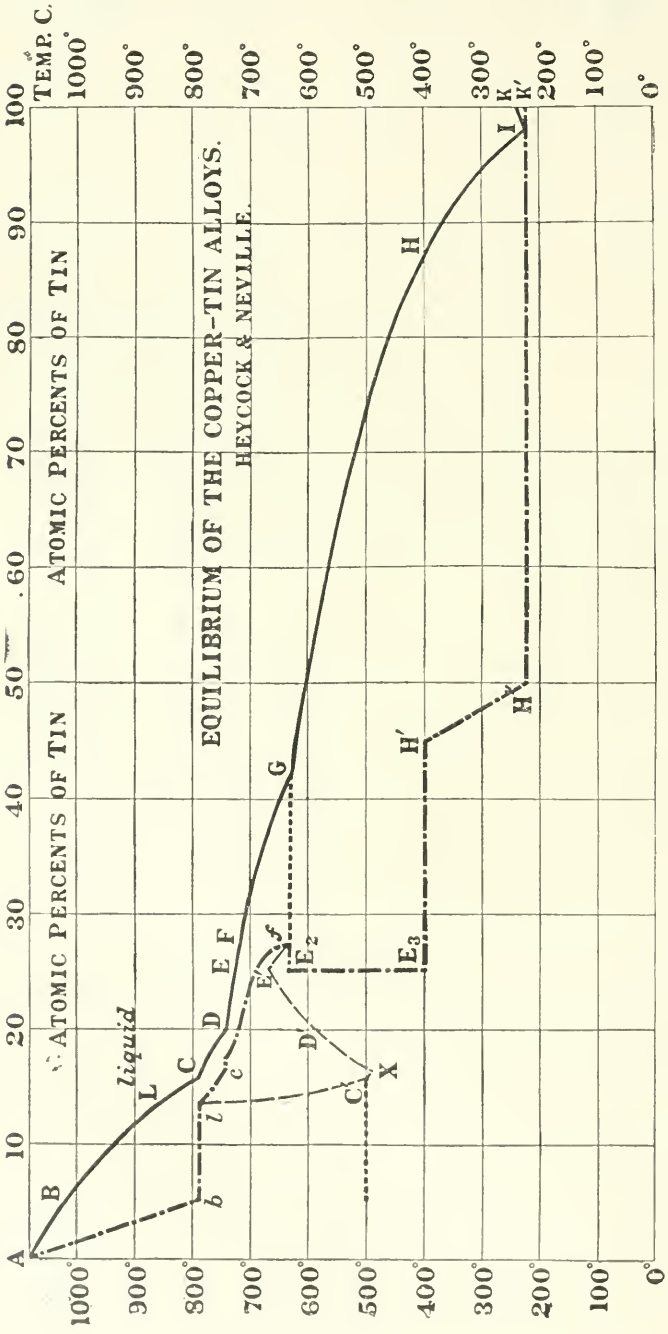
Decarburation of Steels and Thin Metallic Plates by Evaporation in vacuo.—G. Belloc.—In a previous research the author discovered that steel, when heated to about 1000° in a vacuum obtained either from air or hydrogen, is decarburised. His further experiments prove that the decarburation is due to the presence of gases occluded in the metal.—*Comptes Rendus*, cxxxvi., No. 22

ON THE CONSTITUTION OF THE COPPER-TIN SERIES OF ALLOYS.*

By C. T. HEYCOCK and F. H. NEVILLE.

THIS paper is an attempt to fill a very serious gap in the study of alloys. As a rule, an alloy begins to be interesting when the temperature of the liquid alloy has fallen to its freezing-point. This point, which records the moment when solid first appears in the liquid, is easily observed on account of the evolution of latent heat that occurs on the formation of solid, and if the freezing-points of all the alloys of a series are determined, we can plot the freezing-point curve. Many such curves have been traced in the last ten years; that of the copper-tin alloys is given by the upper line in our diagram. The curve consists of several branches cutting each other in angular points. The one thing that these curves record without ambiguity is the number of different solids that can crystallise out of the liquid alloys, for each branch corresponds to the crystallisation of a different substance. Bnt this is almost all that such curves tell us with certainty. They do not tell us whether the solids forming are the pure metals, or pure compounds, or crystalline solid solutions of the metals. Other experiments are needed to decide such questions.

* Abstract of the Bakerian Lecture of the Royal Society, delivered February 26, 1903.



The other great branch of the study of alloys consists in the microscopic examination of the solid alloys after they have cooled to ordinary temperature; that is to say, afterthey have, in general ceased to undergo change. Between these two series of experiments there is an enormous gap of temperature, it may be 1000 or 500 degrees, and it is in this range of temperature that the whole life history of the alloy, regarded as an organism, is to be found. The only fruitful experiments we know of dealing with this intermediate region are the cooling curves of Roberts-Austen and Stansfield. These observers traced automatically the whole of the cooling of the bronzes, and obtained some remarkable results. They found that the evolution of heat at the freezing-point was often succeeded at much lower temperatures by other evolutions of heat, and that many of these must have occurred after the alloy had wholly solidified. These thermal changes point to important chemical or physical changes, though they do not tell us what these changes are. They suggest, however, that the final patterns found by the microscope in the solid alloys are likely to be very complicated, as they may contain several records superposed the one on the other. We found these patterns very beautiful, but hopelessly complicated.

It occurred to us, and this is the method of the paper, that we could simplify the phenomena by a systematic chilling of the ingots at selected temperatures. A number of small ingots of the same alloy were placed in separate tubes in a bath of tin, together with a recording pyrometer, the temperature was raised above the freezing-point of the alloy, and the whole very slowly cooled, the slow cooling being an essential feature of the experiment. Ingots were then extracted at selected temperatures, and rapidly chilled by immersion in water. The microscopic examination of these chilled ingots showed that it was quite easy to distinguish the large crystals, that had formed during the slow cooling preceding the chill, from the matter that was liquid when the ingot was withdrawn from the furnace.

Successive chills of an alloy exhibit the solid growing in amount as the temperature falls, and finally show the ingot completely full of solid. We thus obtain, with very reasonable accuracy, the temperature of complete solidification of the alloy; and by applying the method to alloys with different percentages of tin we have traced a new curve, the "solidus," or curve of complete solidification. The solidus of the bronzes is the second line of the

diagram. It is a remarkable line, made up of sloping, horizontal and vertical branches. As in the freezing-point curve, each branch corresponds to the crystallisation of a different solid.

In the notation of Prof. Roozeboom, the upper curve ABC . . . I, is called the liquidus, because all wholly liquid alloys lie above it; and the solidus, $Ablcdef E_2E_3H'H''I$, is so named because all wholly solid alloys lie below it.

The solidus of the bronzes is remarkable for the very narrow range of temperature within which some alloys pass from the wholly liquid to the wholly solid state.

According to Roozeboom's theory, each sloping branch of the solidus, and there are four such in the diagram, corresponds to the crystallisation out of the liquid of a different series of solid solutions, each vertical part to the crystallisation of a pure body, and each horizontal part to the case of the solid alloy at temperatures immediately below the solidus, being a complex of two substances. Our examination of the chilled ingots has completely verified all these statements.

The evolutions of heat observed by Roberts-Austen and Stansfield at temperatures corresponding to the point C, D, G, and H are due to definite chemical transformations in which one solid is decomposed and another is formed. Chills taken immediately above and below these critical temperatures reveal the nature of each change most clearly.

The transformations at C, D, and especially at H, are very slow, and do not become complete unless the temperature is maintained constant for hours or days at a point slightly below the transformation temperature, but all these temperatures can be made to agree exactly with theory if time is allowed for them. The change at the G temperature is the breaking up of a solid solution into a mixture of the compound Cu_3Sn and liquid, and is instaneous; here we have a case of a solid partially melting as it cools.

The curve 1XE'*f* forms with the part of the solidus immediately above it an area, roughly triangular, within which all the alloys appear to be uniform solid solutions, but, as soon as an alloy cools to the curve, it becomes saturated, and a new body crystallises out of the solid solution. One branch of the curve 1XE'*f* corresponds to the crystallisation of a body rich in copper, the other to the crystallisation of a body rich in tin which is probably the pure compound Cu_4Sn. The angle X (or rather C) is the eutectic angle at which both bodies crystallise together, the whole phenomenon being exactly like crystallisation out of a liquid.

All the results obtained from the study of the chilled alloys are in harmony with the pyrometric work of Roberts-Austen and Stansfield, and many of the changes we have examined correspond to an evolution of heat recorded by them.

The paper is an extension of a short paper published by us in the *Proceedings of the Royal Society*, Dec., 1901.

The Electrolysis of Aqueous Solutions with Platinised Electrodes, and the Electrolytic Formation of Dithionates.—F. Foerster and F. Friessner.—When we electrolyse solutions of sulphuric acid or soda, by means of electrodes covered with platinum black, we observe that the electromotive force of polarisation increases slowly until it reaches 2 volts, or 1·1 volt more than that of a similar voltameter, of which the electrodes have been saturated recently with hydrogen and oxygen gas at the atmospheric pressure. Quantities of oxygen, very small, however, thus brought to the anode, appear to exist there in the dissolved state, and can be utilised for the purpose of effecting certain oxidations. Thus, a solution of neutral sulphite of sodium which, being a bad conductor, does not require the use of a porous diaphragm, is able to give dithionate up to 53 per cent of the original salt if we operate below 1·85 volts with freshly platinised electrodes, and the anode having been previously saturated with oxygen by electrolysis for forty hours, from NaHO with a current of 0·25 ampère.—*Berichte*, vol. xxxv., p. 2515,

A NEW METHOD FOR THE QUALITATIVE AND QUANTITATIVE ANALYSIS OF OSMIDES OF IRIDIUM.

By MM. LEIDIÉ and QUENNESSEN.

During the examination of the process used by MM. Sainte-Claire Deville and Debray for the analysis of osmides of iridium, we have made a certain number of observations. Thus, when the product of the attack of the osmides by binoxide of barium is treated with dilute acids there is a disengagement of peroxide of ruthenium, which is volatilised at the same time as the peroxide of osmium. Again, in the separation of the iridium and ruthenium, the precipitation of Ru_2Cl_6 by chloride of ammonium cannot be complete, and when we have treated the metals which result from the calcination of the insoluble double chlorides with fused potash and nitrate of potassium, a portion of the iridium may dissolve in water with the ruthenium, so that the binoxide of ruthenium precipitated by acids may carry binoxide of iridium with it. Finally, they estimate the osmium by difference, by driving it off in the form of peroxide, so that they have nothing to check the weight of this element but the estimation of the numerous impurities contained in the osmides.

The method we are about to give is an application of our previous researches. It is based on the action that fused binoxide of sodium has on the metals of the platinum group (*Bull. Soc. Chim.*, [3], vol. xxvii., p. 179), and on the analytical properties of the double nitrites of these metals (*Comptes Rendus*, vol. cxxxi., p. 888; *Bull. Soc. Chim.*, [3], vol. xxv., p. 9).

I. *The Attack of Osmide of Iridium.*

As it is exceptional, even in the residues from the attack of platinum ores, to find osmides in a sufficiently finely divided state to be attacked directly, and as the osmides, in their usual condition, resist all reagents and cannot be pulverised, it is necessary first to decompose them. For this purpose we use the old method employed by Sainte-Claire Deville and Debray, eliminating the zinc from the alloy by heat, as they did, its elimination by means of hydrochloric or sulphuric acids is not to be recommended; the former dissolves the platinum metals, the latter leaves an alloy of zinc which may deflagrate in the presence of binoxide of sodium.

Thus we melt, in a nickel crucible, 10 grms. of hydrate of sodium (previously fused), and into this we gradually throw an intimate mixture of 10 grms. of osmide of iridium and 40 grms. of binoxide of sodium; this must be stirred continuously with a nickel spatula, and heated sufficiently to keep the mixture in a semi-fluid condition. The operation should not last more than about half-an-hour. The addition of soda has for its object the lowering of the fusing-point of the binoxide, and of diminishing considerably the attack on the crucible. The material is run out on a sheet of nickel. When cold it is broken up, and thrown in small portions at a time into a porcelain crucible covered with a funnel, and containing a litre of water; the portion adhering to the crucible is also treated with water. All the liquors are added together, and when cool they are left to stand in decantation flasks with ground stoppers. The clear liquor is decanted, and the insoluble residue taken up with hypochlorite of soda diluted with its own volume of water to dissolve the binoxide of ruthenium which might be formed by decomposition brought about by the water. The wash waters are added to the original solution.

The solution thus obtained contains all the osmium and ruthenium in the form of osmiate and rutheniate, with the greater portion of the iridium in the form of iridiate. It may contain also traces of gold and palladium, as well as chromium, aluminium, and manganese from the ore, in the form of alkaline salts. The insoluble portion contains the remainder of the iridium, the iron from the ore, and the nickel from the crucible, with sometimes traces of platinum and rhodium.

II. *Separation of Osmium and Ruthenium.*

The solution is placed in a glass retort of which the drawn out neck is fitted into the neck of a flask having a lateral tube, the central tube forming a hydraulic joint; such a flask is similar to the one used for the condensation of peroxide of ruthenium (Joly, "Encyclopædie Chimique de Frémy," vol. iii., No. 3, p. 236)). This flask is followed by two similar ones forming the condensing apparatus. They are all three plunged into iced water, and two-thirds filled with hydrochloric acid diluted with two volumes of water: by grinding all the joints with emery, all loss of condensible vapours is prevented. The two first flasks will probably be sufficient, the third acts as a control. A current of chlorine is passed through the retort, cold at first, then when the liquid commences to give off bubbles of oxygen, it is heated to about 70°. The osmium and ruthenium are transformed into volatile peroxides, OsO_4 and RuO_4, which condense in the flasks, the iridium into sesquichloride, which remains in the retort in solution, thanks to the excess of soda. The contents of the retort should remain alkaline until the end of the distillation, first on account of the action of hydrochloric acid on RuO_4, and afterwards because the chlorine passing through the cold recipients, gives hydrate of chlorine which obstructs the tubes. (It is this hydrate that Joly must have mistaken for an emulsion of RuO_4). If by chance the contents of the retort become acid, soda must be added. The end of the operation can be determined by making sure that the drops, which distil over, do not blacken a solution of sulphuretted hydrogen.

Under the influence of hydrochloric acid, the peroxide, RuO_4, is transformed into the sesquichloride, Ru_2Cl_6, which is stable; while the peroxide, OsO_4, does not undergo any change. This reaction, commencing in the cold, ought to be completed by the action of heat. For this purpose the contents of the three flasks are placed together in a retort, connected with a system of three condensers similar to those in the preceding apparatus. The flasks are plunged into ice, they are filled up to two-thirds, the first with hydrochloric acid diluted with two volumes of water to arrest the incompletely transformed peroxide, RuO_4; the two others are filled with a solution of soda at 12 per cent of NaOH, treated with 2 per cent of alcohol, to transform the peroxide, OsO_4, into osmiate of sodium. The contents of the flask are heated to about 70°, while passing a slow current of air. When no more peroxide of ruthenium distils over (the drops distilled should not colour hydrochloric acid brown), the contents of the first condensing flask are returned to the retort, and the flask is filled up to two-thirds with an alkaline alcoholic solution like that in the next two flasks. The distillation is then pushed to its completion; that is to say, until the drops no longer blacken sulphuretted hydrogen; as a rule, to obtain this result, it is necessary to distil half the contents of the retort. The osmium is then contained entirely in the condensing flasks, in the form of osmiate, and the ruthenium is in the retort in the form of sesquichloride; these two compounds not being volatile are easily determined in subsequent operations.

To make certain that the separation of the Os and Ru is complete we proceed in the following manner:—A solution containing OsO_4 and RuO_4 becomes brown under the influence of hydrochloric acid, owing to the formation of brown Ru_2Cl_6. A solution containing Ru_2Cl_6 and OsO_4, treated with carbonate of baryta, freshly prepared and free from baryta, gives a precipitate of Ru_2O_3; the solution, freed from the chloride of barium formed by means of SO_4Na_2, should not become violet in the presence of an alcoholic solution of soda (formation of violet osmiate).*

* We propose to substitute this method for the separation of osmium and ruthenium for that of MM. Sainte-Claire Deville and Debray, adopted at first by M. Liedié, and which figures as his general method for the extraction and separation of the metals of the platinum group. (See above).

III. *Separation of Iridium.*

The contents of the retort from which the osmium and ruthenium have been driven in the first distillation, are acidulated with hydrochloric acid. The residue, insoluble in water, resulting from the attack of the osmide by Na_2O_2, is dissolved in hot dilute hydrochloric acid; this residue is easily soluble, while the other methods of attack (potash and nitrate of potash, for example) give a mass which is very difficult to dissolve, even with aqua regia. If any crystals of unattacked osmide are found, owing to their being insufficiently finely divided, they must be collected and subtracted from the original weight. The two solutions are united; the solution then contains all the iridium, as well as the iron in the ore, and the nickel from the crucible; it may contain traces of gold also, as well as rhodium and platinum, and any other foreign metal associated with the osmide, such as chromium, aluminium, silicon, manganese, copper, &c. The solution is heated, and to precipitate all the foreign metals, it is treated successively with nitrite of sodium and carbonate of sodium, following the instructions given by one of us *à propos* of the general method for the separation of the metals of the platinum group (Leidié, *Comptes Rendus*, vol cxxxi., p. 888; *Bull. Soc. Chim.*, [3], vol. xxv., p. 9). Nothing remains in solution but the double nitrite of iridium and sodium; this is transformed into chloroiridiate by warm hydrochloric acid. Then, as the large amount of chloride of sodium present in the solution might be prejudicial, either to the precipitation of the chloroiridiate by chloride of ammonium, or to the precipitation of the iridium by magnesium, the cooled solution must be saturated with hydrochloric acid gas. The precipitated chloride of sodium is drained and washed with hydrochloric acid; the solutions, which only contain chloroiridiate of sodium with a little chloride of sodium, are added together.

IV. *Estimation of the Metals.*

Osmium.—The contents of the flasks containing the osmiate of sodium are added together (if they are not decidedly violet they must be heated gently), and strips of aluminium are plunged in; the osmium is deposited in the metallic form, while the aluminium dissolves in the soda. Care must be taken not to add too much aluminium at first, as the alumina formed, not finding a sufficient quantity of soda to enable it to go into solution, would precipitate an aluminate which is very difficultly soluble both in acids and in alkalis. When the solution is once decolorised, the precipitated osmium, which is very dense, is washed by decantation, first with water to remove the aluminate of soda, and then with 5 per cent sulphuric acid to remove the remaining excess of aluminium, along with the iron accompanying this metal.

This osmium is thrown on an asbestos filter connected with a filter-pump and well-washed; the filter must have been treated first with 20 per cent sulphuric acid, then washed, dried, calcined at a red heat, and weighed in a closed tube. The osmium is dried in a bell-glass filled with hydrogen, then heated to dull redness, and cooled in a current of this gas; the hydrogen is only driven off by the carbonic acid when the whole has been cooled, as the latter gas oxidises the osmium when hot. The filter is weighed again in a closed tube.

As a check, the osmium may be driven off in the form of the peroxide, OsO_4, by heating the filter to redness in a current of oxygen, and then weighing it again.

Ruthenium.—The hydrochloric solution containing the sesquichloride, Ru_2Cl_6, is evaporated gently to a syrupy consistence, so as to drive off the excess of acid. The residue is taken up with 50 or 60 c.c. of water, and a few fragments of magnesium added gradually; the solution becomes clear and takes a blue tint; this reaction is characteristic of ruthenium, and was wrongly attributed to osmium by Fischer, the latter being completely decolorised. The solution is then decanted, and the powder is washed with 5 per cent sulphuric acid, so as to remove the excess of magnesium. Throw on a filter, wash with water, dry,

and after incinerating the filter at the lowest possible temperature, heat the whole in hydrogen to a red heat, then allow to cool in carbonic acid, and weigh.

Iridium.—The solution containing the chloroiridiate of sodium is evaporated to drive off the large excess of hydrochloric acid present. The residue is taken up with water, and diluted to a volume of 500 c.c. From this we take 50 or 100 c.c., according to the probable proportion of iridium present, and add gradually some fragments of magnesium until it is completely decolorised. The powder is washed with 5 per cent sulphuric acid, then with water, and dried; after the incineration of the filter, it is heated to redness in hydrogen, cooled in a current of carbonic acid, and weighed.

In all these operations we use sulphuric acid rather than hydrochloric acid, which would dissolve a portion of the precious metal.

V.

Analyses conducted in this manner have been carried out on osmides from various sources. M. Riche, Directeur des Essais, at the Hôtel des Monnaies, has been good enough to supply us with osmides resulting from the operations to which gold is subjected during purification. In these osmides we have never met with any but the four following metals :—Iridium, osmium, ruthenium, and iron. On the other hand, in osmides from the residues from the treatment of the metals of the platinum group, we find traces of these latter metals, as well as the commoner ones accompanying the ore; the separation of the precious metals is made then by the general method which has been given already by one of us (Leidié, see above).

It would seem thus to be well established, as MM. Sainte-Claire Deville and Debray were inclined to believe, that when osmide of iridium is perfectly freed from the metals of the platinum group with which it is often mixed; it does not contain any other metals than the four we have just mentioned above.

A METHOD OF EXTRACTING COPPER FROM ITS SULPHIDE ORES.*

By GUSTAVE GIN.

Dissolved sulphurous acid possesses the known property of attacking oxide and carbonate of copper, forming an unstable sulphite of the binoxide, which is gradually transformed into a mixture of cuproso-cupric sulphite and sulphate, according to the reaction—

$$(1).\quad 3CuO + 3SO_2 = 3SO_3Cu.$$

$$(2).\quad 3SO_3Cu + CuO = \underset{\text{Cuproso-cupric sulphite.}}{SO_3Cu_2,SO_3Cu} + \underset{\text{Sulphate of copper.}}{SO_4Cu}.$$

Cuproso-cupric sulphite is slightly soluble in water, but easily soluble in solutions of sulphurous acid or cupric sulphate.

On heating the solution to 180° (under a pressure of 10 kilogrms.) it loses sulphurous acid, while cupric sulphate and metallic copper are formed :—

$$(3).\quad (SO_3Cu_2 + SO_3Cu) = 2Cu + SO_4Cu + SO_2.$$

If we group the formulæ 1, 2, and 3 together we see that, taken altogether, the reactions correspond to $4CuO + 2SO_2 = 2Cu + 2SO_4Cu$; that is to say, that half the copper can be obtained in the metallic state, and the other half in the form of sulphate.

On the above principles I have devised a process for the treatment of copper ores, utilising the sulphurous acid produced by roasting them in such a manner that the active reagents may be extracted entirely from the ore itself and from the atmosphere.

The ore is roasted in such a manner that the whole of the sulphide of copper is transformed into binoxide or sulphate, and the whole of the iron into peroxide.

Then it is lixiviated methodically by means of a solution of sulphurous acid prepared in the ordinary manner. A saturated solution of cuproso-cupric sulphite and sulphate of copper is obtained, containing at the same time a certain proportion of sulphite and sulphate of protoxide of iron. The sulphite of the sesquioxide of iron in the presence of an excess of sulphurous acid is transformed according to the reaction, $SO_2,Fe_2O_3 + SO_2 = SO_4Fe + SO_3Fe$.

The saturated solution of the salts of copper and iron is pumped into a copper boiler, where it is heated up to 180°, by which it is expected a pressure of 10 kilos. is produced. At this temperature the sulphite and the ferrous sulphate are completely insoluble, and are precipitated. As for the cuproso-cupric sulphite, it is dissociated and loses two-thirds of its copper in the metallic state, and at the same time sulphate of copper is formed.

The cloudy liquid is forced by its own pressure through a filter-press heated by steam circulating round the plates, an apparatus I patented some time ago for the mechanical separation of cupric and ferrous sulphates, but which could be replaced by any other arrangement for the filtration of solutions at a high temperature.

In this manner we obtain a solution of sulphate of copper which can be cemented or treated for crystallised sulphate, and a precipitate containing metallic copper, and sulphite and sulphate of the protoxide. This precipitate is washed with pure water, which becomes saturated with sulphate of protoxide of iron, which may be extracted by crystallisation.

The residual sulphite is then oxidised by moist air, and gives sulphate of the protoxide, which can be eliminated by a fresh washing, and there remains finally metallic copper of great purity, which is melted and run into ingots.

* A Paper read at the Fifth International Congress of Chemistry at Berlin. Section III.

INFLUENCE OF THE NATURE OF THE CATHODE ON THE QUANTITATIVE SEPARATION OF METALS BY ELECTROLYSIS.

By A. HOLLARD.

In electrolytic analysis the metals are divided into two principal classes, according to whether they are or are not capable of being deposited on the cathode from a strongly acid solution. The metals which will not deposit in strongly acid solutions are those which require, for covering the cathode, electric tensions higher than the tension at which hydrogen commences to be given off. We see thus that, under the influence of these high tensions, a strongly acid solution (that is to say, a solution in which the proportion of H^+ ions is very high) gives rise to a disengagement of hydrogen at the cathode so abundant that all metallic precipitation becomes impossible thereon.

The metals which are capable, on the other hand, of depositing on the cathode in strongly acid solutions are those which require for this precipitation, tensions lower than the tension of polarisation of hydrogen; their deposition therefore is not interfered with by the hydrogen.

If we call the tension of polarisation of hydrogen zero, we shall have the following values for the tension of polarisation of the principal metals (Nernst and Wilsmore, *Zeit. f. Elektrochemie*, November 8, 1900).

As can be seen, the classification of the metals into two groups, has for its basis the position occupied by hydrogen in the table of the tension of polarisation of the metals. But this position is only fixed in practice in electrolytic analysis if we always use platinum cathodes. As a matter of fact, hydrogen—as has been shown by Caspari (*Zeit. fur Physik. Chem.*, 1899, vol. xxx., p. 89)—has a tension of polarisation which is variable with the metal constituting the cathode. If, therefore, we use, as we have done, cathodes formed of other metals than platinum,

the tension of polarisation of hydrogen takes another position in the accompanying table; this causes a certain number of metals to pass from one group to the other.

Table I.

Metals not Deposited in Strongly Acid Solutions.

Zn	+0·77
Cd	+0·42
Fe	+0·34
Co, Ni	+0·23
Sn	+0·19
Pb	+0·15
H	0·00

Metals Deposited in Strongly Acid Solutions.

As	−0·29
Cu	−0·33
Bi	−0·39
Sb	−0·47
Hg	−0·75
Ag	−0·77
Pd	−0·79
Pt	−0·86
Au	−1·08

It is conceivable, therefore, that, by the choice of a suitable metal for the cathode, we may succeed in separating two metals of the same group, of which the tensions of polarisations are too near together to enable us to separate by means of a platinum cathode. For this purpose it suffices to choose a metal for the cathode which gives hydrogen a tension of polarisation between those of the two metals to be separated. The element whose tension of polarisation is the lowest will be precipitated then alone in a strongly acid solution.

For choosing the most suitable metal for the cathode, the following table must be consulted; it was drawn up by Caspari, and gives the different values of the tension of polarisation of the hydrogen set free on different metals used as the cathode in a solution of normal sulphuric acid.

Table II.

Pt, platinised	0·00
Au	0·02
Fe (in NaOH)	0·08
Pt, polished	0·09
Ag	0·15
Ni	0·21
Cu	0·23
Pd	0·46
Cd	0·48
Sn	0·53
Pb	0·64
Zn (in acid solution of zinc)	0·70
Hg	0·78
Cu (amalgamated)	0·51
Pb „	0·54
Cd „	0·68

But it is not sufficient, however, to choose for the cathode a metal that has the property of raising the tension of polarisation of hydrogen above that of the metal to be precipitated, for this property of the metal constituting the cathode disappears at the moment it is covered by the precipitated element, and then the cathode plays the same part as if it were made exclusively of the metal precipitated. It is therefore necessary, further, for the continuation of the precipitation, that the latter metal also should have the property of raising the tension of polarisation of hydrogen above its own tension of polarisation.

By using cathodes formed of the same metal that it is proposed to deposit, we see from the preceding table that we can precipitate from strongly acid solutions, not only the metals of which the tensions, in Table I., are lower than that of hydrogen, but also lead, tin, and cadmium. In fact, the tension of polarisation of lead (+0·15) is decidedly lower than that of hydrogen liberated on a lead cathode (+0·64); the same holds good with tin and cadmium.

As an example of the application of this new method of analytical separation, we will describe the separation of zinc and cadmium—metals that we have been unable to separate when using a platinum cathode,* on account of the closeness of their tensions of polarisation. On the other hand, we have been able to effect their separation with either a cadmium or tin cathode in a very acid bath. Our cadmium and tin cathodes were nothing more than platinum-gauze electrodes, covered electrolytically with cadmium or tin.

The cadmium and the zinc, brought into solution in the state of sulphates, were treated with 10 grms. of sulphate of ammonia and an excess of 5 c.c. of concentrated sulphuric acid. The solution, diluted to 300 c.c., was electrolysed with a current of 0·3 ampère. The following results were obtained:—

Experimental Results.

Amount weighed.† Cd. Grm.	Amount weighed.† Zn. Grms.	Cd deposited. Grms.
On a Cathode of Tinned Platinum-gauze.		
0·1991	2	0·1972
0·2996	2	0·3010
0·1996	1	2·002
On a Cathode of Cadmium-plated Platinum-gauze.		
0·1991	2	0·1984
0·2488	2	0·2484
0·1991	0	0·1968
On a Cathode of Platinum Gauze.		
0·2000	2	0·0002

—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 6.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, June 17th, 1903.

Prof. W. A. Tilden, D.Sc., F.R.S., President, in the Chair.

Messrs. E. S. Beaven and C. Rawson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messers. Percy W. Gent, 792½, Ridge Street, Newark, N.J., U.S.A.; Henry William Lawrence, Wellington, New Zealand; Herbert Stanley Redfern, B.Sc., Ningpo, China; Frank Gurney Smith, 7, Luxemburg Gardens, Brook Green, W.

Presentation of the Longstaff Medal.

The President spoke as follows:—We have so recently celebrated the Centenary of the Atomic Theory that it is a matter of interest to notice that, in the award of the Longstaff Medal on the present occasion, we honour the practical fulfilment of the deductions from that great conception. Dalton himself represented in his diagrams atoms of solid bodies like ice arranged with reference to the crystalline form of the solid, but for three-quarters of a century

* Both in slightly acetic solutions and in cyanide solutions and no matter how small the current used.

† The cadmium used in the first three experiments contained:—Pb=0·231 per cent, Fe=0·000 per cent, Zn=0·000 per cent. The cadmium used in the next three experiments contained:—Pb=0·245 per cent, Fe=0·193 per cent, Zn=0·000 per cent. This amount of impurity has been subtracted from the amounts actually weighed, and it is the differences thus obtained that figure in the column "Amount weighed."

successive writers could merely speculate as to their possible order in space of three dimensions. The discoveries of Pasteur in connection with hemihedrism in crystals, and the study of the lactic acids by Wislicenus, prepared the way for the development of the theory of stereo-chemistry by van 't Hoff and le Bel in 1874. But while that theory has prospered and has led to innumerable developments in the study of the compounds of carbon, and although it must have been always obvious that if the idea of a tetrahedral configuration was valid for compounds of one element a corresponding idea should be equally applicable to those others, the demonstration of the facts upon which such a development must rest has only been accomplished within the last four years.

To Professor William Jackson Pope the Council has awarded the Longstaff Medal by a unanimous vote, for his researches on the stereo-chemistry of compounds of elements other than carbon. In 1893, Professors Kipping and Pope prepared the *d*-bromo- and *d*-chlorocamphorsulphonic acids, and by the use of these and other powerful optically-active acids, Mr. Pope has succeeded, not only in resolving into their active components certain racemic bases which had been found irresolvable by the use of tartaric acid, but in 1889, by the use of *d*-camphorsulphonic acid, he separated the dextro- and lævo-modifications of a synthetical tetralkylammonium base, and thus definitely established the existence of asymmetric optically active nitrogen compounds.

Since that time, by similar methods, he has obtained the dextrorotary methylethylthetine, a dextrorotatory tin compound, and both forms of a selenetine, thus demonstrating the fact that the elements nitrogen, sulphur, tin, and selenium are each capable, like carbon, of producing asymmetric combinations possessing optical activity. We therefore now possess direct experimental evidence in regard to the compounds of carbon, tin, sulphur, and selenium, as tetrad elements, and of nitrogen as a pentad, so that it may confidently be expected that not only will the phosphorus series of elements be found capable of producing pairs of enantiomorphous compounds, but, possibly, similar modifications of oxonium bases may be discovered, and some of the metals, such as platinum, cobalt, and chromium, may be found to exhibit similar phenomena. The doctrine of valency, no less than the doctrine of atoms, in its application to all ordinary terrestrial chemical phenomena, is thus triumphantly established.

Professor Pope, it gives me great pleasure to be the medium of communicating to you the congratulations of the Council, and in handing you the Longstaff Medal I express the feelings of the whole chemical world when I say that we trust you will have health, and strength, and time to continue the researches which have already yielded such a rich harvest of splendid results.

Professor Pope, in expressing his sense of the honour done him by the award of the Longstaff Medal, desired to acknowledge gratefully the assistance which the Research Fund Committee had given to his work; it would be difficult to over-estimate the extent to which the Research Fund of the Chemical Society has contributed to the encouragement of chemical investigation in Great Britain. He wished also to record his indebtedness to his old friend and teacher, Dr. H. E. Armstrong, who first taught him to look upon our science as a living and growing branch of knowledge, and inspired him with a desire to contribute something towards its development.

Dr. G. B. Longstaff, in expressing his great pleasure at being present on this occasion, said that the researches for which Professor Pope had been awarded the medal considerably advanced our conceptions of the atomic theory in so far as they broke down some of the apparent barriers between carbon and the other elements. He recalled the fact that his father, who had been a friend of Dalton's, was not only a Fellow of this Society from its commencement, but also the founder of Chemical Societies in Edinburgh and Glasgow, and was, moreover, instrumental in placing on a working basis the Research Fund (first suggested by Dr. Millar) to which Professor Pope had referred. Nevertheless, the name of the donor of the medal would have remained obscure except for the reflected light thrown on it, as it were, by the great names of an already long succession of eminent medallists.

A ballot for the election of Fellows was held and the following were subsequently declared duly elected:— Henry James Aubrey; George Barger, B.A., B.Sc.; Colin Noel Bennett; Wilfrid W. O. Beveridge; Charles Drake Bibby; Henry J. W. Brennand, B.A., M.B.; William Godsell Burghard; Ernest Bury, M.Sc.; Thomas Campbell; Albert James Carrier, B.Sc.; Edwin Jesse Fairhall; William Hunter Gandy; Francis Gerald Harmer; Frank William George King; Henry Wolff Levy; John Howard Linday; Charles Edwin L. Livesey, B.Sc.; John Christopher Mann; Alfred Ernest Moore, B.A., B.Sc.; Arthur Moore; George Marshall Norman, B.Sc.; George Harry Parry; Charles Stanley Purcell; Thomas Rhind, M.R.C.S.; Charles Joseph Smith; James Cruickshank Smith, B.Sc.; Dennis Tyrrell; Norbert Van Laer; Sydney H. Woolhouse, M.A., B.Sc.

Of the following papers those marked * were read:—

*96. "*The Estimation of Arsenic in Fuel.*" By T. E. Thorpe.

An account was given of a method of estimating the amount of arsenic in fuels which is accurate, fairly rapid in execution, and which has the additional merit of directly distinguishing been the arsenic which is volatilised on burning the fuel and that which remains fixed in the ash. The process consists simply in burning a known quantity of the finely powdered coke or coal in a stream of oxygen, passing the products of combustion through a suitable absorbing apparatus, and determining the amount of arsenic so absorbed as well as that left in the ash.

The estimation of the arsenic in the solutions may be made by means of the Marsh apparatus and comparison with standard deposits of arsenic, or preferably with the electrolytic method described in the subsequent communication. The accuracy of the method was tested by burning fuels containing known quantities of arsenic, added in the form of arsenical pyrites.

*97. "*The Electrolytic Estimation of Minute Quantities of Arsenic, more especially in Brewing Materials.*" By T. E. Thorpe.

An electrolytic method for detecting arsenic appears to have been first suggested by the late Prof. Bloxam (*Quart. Journ. Chem. Soc.*, 1861, xiii., 12 and 338), but in its original form it had several disadvantages which have prevented it from being generally adopted by chemists. The process has been carefully investigated in the Government Laboratory, and in the form described in the present communication it is easy of application, and is capable of giving trustworthy results with a comparatively small expenditure of time and trouble.

The test may be applied to malt and malt substitutes, wort, hops, and hop substitutes, beer, yeast and yeast foods, finings, &c.

The advantages of the electrolytic method are:—

1. That it obviates the use of zinc.

2. It is simple in execution, is under perfect control, and may be carried out under such conditions that the results obtained by different operators are strictly comparable, inasmuch as with a current-strength of fair regularity the evolution of the gas is practically constant and uniform.

3. The whole of the solution to be tested for arsenic may be added to the apparatus at once, so that during the whole time of testing the arsenic is under the influence of the "nascent" hydrogen.

4. It has been established that such amounts of arsenic as are present in beer or its ingredients are evolved as hydrogen arsenide during the thirty minutes occupied by the test. The nature of the material associated with the arsenic is found to exercise no inhibiting effect on the

formation and evolution of the hydrogen arsenide. Aqueous extracts of malts and worts may be added directly to the electrolytic apparatus without previous destruction of the organic matter as required by the zinc and acid process.

5. The deposits obtained are more uniform in character than those furnished by the zinc and acid method, and admit therefore of more accurate quantitative comparison.

6. The process allows of the simultaneous execution of a number of estimations of arsenic, depending upon the arrangement of the rheostat.

The disadvantages of the method are :—

1. The initial cost of the apparatus as compared with that employed in the zinc and acid method.

2. That it can only be applied when an electric current of sufficient intensity is available.

Discussion.

Dr. Thorne said the electrolytic process would prove of the greatest value to the large number of chemists who had to test for very small quantities of arsenic. The Marsh-Berzelius process was very reliable and accurate, and had been rightly recommended by the Committee of the Societies of Chemical Industry and Public Analysts, but those who used it knew the difficulty of obtaining zinc and hydrochloric acid free from arsenic, and hence these reagents must be carefully purified if the test was to be satisfactorily carried out. In the process just shown, these difficulties were obviated. He had had the opportunity of seeing the method in operation, and could therefore speak as to its satisfactory working.

Mr. Arthur R. Ling also thought that the electrolytic process would doubtless prove much more convenient than the Marsh-Berzelius method, which, in the case of many materials, necessitated the destruction of organic matter.

In the set of standards exhibited, the mirrors obtained in the presence of glucose appeared to be less intense than those produced in the absence of organic matter, from the same weight of arsenic, by the Marsh-Berzelius method.

Mr. William Thomson believed that the electrolytic method suggested by Lord Kelvin and the ingenious apparatus devised by Dr. Thorpe and his colleagues may ultimately afford the most practicable means of detecting arsenic in beer and food-stuffs.

He had tested one of the appliances, and had found that it would not detect the presence of more than about 1/350th of a grain of As_4O_6 per gallon, whilst the zinc and acid method easily detects 1/1000th of a grain per gallon when using 50 c.c. of the solution. Assuming at first that this difference was due to an insufficient surface of cathode, he used a much larger area of platinum wire gauze, but obtained the same results with regard to the size of mirrors as those obtained in Dr. Thorpe's apparatus.

Platinum seems to retain minute quantities of arsenic, but when a pure zinc cathode is employed the 1/1000th part of a grain per gallon can easily be detected when using 50 c.c. of the solution.

He could confirm Dr. Thorpe's observations that minute quantities of arsenic in the form of pentoxide cannot be detected by the electrolytic method, 1/200th of a grain per gallon (using 50 c.c.) yielded no mirror at all with the platinum anode, and gave an approximately half-sized mirror with the zinc anode.

In other respects, his results differed from those obtained by Dr. Thorpe. He found that both amyl alcohol and sugar seriously reduce the size of the mirrors, and he was of opinion that it is unsatisfactory to test beer directly in Dr. Thorpe's apparatus.

Dr. MacGowan said that, together with Mr. R. B. Floris, he had during the past year examined a large number of samples of anthracite for arsenic. The method which, after some preliminary experiments, they had employed in this work was a modification of Newlands and Ling's basic process. Although the results obtained were very consistent, and, as they believed, accurate, yet this process had the disadvantage of being an indirect method with regard to the "volatile" arsenic present. Other things being equal, a direct method such as that now brought forward by Dr. Thorpe was preferable.

Dr. Thorpe, in reply to Mr. Ling, stated that he had not been able to perceive any difference in the intensity of the mirrors produced from a known quantity of arsenic in the electrolytic method as compared with the Marsh-Berzelius method. A comparison of the standards in the two cases, as shown on the table, would prove that there was no practical difference in the two series.

In reference to what fell from Mr. Thomson, he might say that attempts had been made to increase the activity of the cathode by depositing platinum black upon it, but nothing seemed to be gained thereby. Experience showed that the best and most uniform results were obtained by keeping the metallic surfaces as clean and bright as possible.

*98. "*Crystallised Ammonium Sulphate and the Position of Ammonium in the Alkali Series.*" By A. E. H. Tutton.

The author has hitherto shown that the morphological and physical properties of the crystals of the normal sulphates and selenates of potassium, rubidium, and cæsium follow the order of progression of the atomic weights of the three alkali metals. An analogous study of normal ammonium sulphate indicates that this salt stands in the series of normal alkali sulphates between rubidium and cæsium sulphates, and very close to the rubidium salt, as regards the following nine properties :—Solubility, molecular volume, distance ratios (topic axes), refractive indices, axial ratios of the optical ellipsoid, molecular refraction along axial directions, mean refraction equivalent both for the crystallised and the dissolved salt, and the general optical scheme which governs the optic axial angle phenomena. With respect to all these properties, the replacement of the two atoms of potassium by the ten atoms composing the two NH_4 groups is accompanied by an effect but slightly greater than when two atoms of rubidium are substituted for those of potassium.

The specifically different nature of the ammonium radicle as compared with a metallic atom of the alkali group asserts itself in regard to the morphological angles and axial ratios, the specific refraction, certain details of the distance ratios and the optic axial angle phenomena, and in the development of only one instead of two cleavages. Yet even in the case of the crystallographical angles, this difference is only manifested with regard to the direction of the change of angle on replacement, and as far as the amount of change is concerned the ammonium compound stands between the rubidium and cæsium salts, and somewhat nearer to the latter. It is, indeed, surprising that the introduction of eight additional atoms should be accompanied by less change in the exterior angles of the crystals than when an exchange of cæsium for potassium atoms occurs.

In short, the specific constants indicate the peculiar nature of the ammonium radicle, whilst the molecular constants show that ammonium occupies a place in the alkali series immediately after rubidium.

This result opens up questions of the arrangement of the atoms in the molecule, and the closeness of the packing of the molecular structural units in the crystal edifice. It suggests that either the atoms have a range of motion inside the molecular dimensions sufficiently wide to admit eight more atoms without altering those dimensions to an appreciably greater extent than when the transposition of rubidium and potassium atoms is effected, or that the structural units are so loosely packed, that is, the amount of free space is so large as compared with the amount of matter in the whole space defined by the distance ratios, that there is adequate room for the increase of the material part of the molecule by eight atoms, without separating the centres of contiguous molecules more than when a simple metallic interchange occurs.

*99. "*The Action of Hydrogen on Sodium.*" By A. Holt, jun.

Pieces of sodium, free from oil were placed in a nickel boat and heated in a combustion tube through which a slow current of pure dry hydrogen was passing. An ordinary small combustion furnace without top tiles was employed, and it was arranged so that, whilst the lower part of the tube was strongly heated, the upper portion was kept at a lower temperature in order that the hydride might condense on it. The hydride thus obtained consisted of colourless matted crystals, a hairy deposit not unlike cotton-wool, and a white powder deposited next to the glass. The hairy material was formed on and above the powder in front of the boat, whilst the crystals projected from the surface of the tube at either side of the boat.

The analysis was performed (1) by decomposing the hydride with dry, air-free hydrogen chloride, collecting the hydrogen due to the reaction, and estimating the sodium chloride formed by titration with silver nitrate; (2) by decomposing the hydride with absolute alcohol, collecting the hydrogen evolved, and estimating the sodium in the alcoholic solution by titration with standard acid. The ratio of sodium to hydrogen showed that the hydride had the composition NaH, as already stated by Moissan.

The hydride was instantly decomposed by water, forming sodium hydroxide and hydrogen, this result also occurring in air after a few minutes; it was at once decomposed by hydrochloric acid, the decomposition being accompanied by flame and a detonation. The hydride was immediately attacked by nitric and sulphuric acids, hydrogen sulphide, and alcohol, but ether, benzene, and mercury were without action on it.

With phenol and ammonia, it reacts only when heated, forming sodium phenoxide and sodamide respectively.

Carbon dioxide, when perfectly dry, has no action on the hydride at the ordinary temperature, but on heating, a reaction takes place with the formation of carbon and a carbonate. The partially dried gas reacts with the hydride at the ordinary temperature, yielding a formate and carbon. When heated with ferric oxide, the hydride gives a ferrate.

The combination of hydrogen with sodium appears to take place only when the latter is in a state of vapour; the sodium probably interacts only when it is partially monatomic.

100. "*The Action of Halogens on Compounds containing the Carbonyl Group.*" By Arthur Lapworth.

Although bromine acts very slowly on a dilute aqueous solution of acetone, yet, in presence of alkali, bromination occurs readily. It is now found that acids also accelerate the speed of substitution to an extent which depends mainly on the concentration of the hydrogen ions, although the nature of the anion appears to have some influence.

In the author's experiments, the concentration of the bromine was always considerably less than that corresponding with one molecular proportion, and at constant temperature the velocity with which the bromine disappeared was nearly independent of its concentration. With sulphuric acid between the concentrations 0·4 N and 0·04 N, the velocity increased somewhat less rapidly than the concentration of the acid, but slightly more rapidly than that of the acetone. The relative velocities of reaction with 0·4 N sulphuric, nitric, and hydrochloric acids were about 1·19 : 1·20 : 1·36. The velocity was not affected if the acetone was left in contact with the dilute acid for several days before the introduction of the bromine.

Preliminary experiments with chlorine indicate that in presence of much acid it is removed at about the same speed as bromine.

These facts confirm the view that the bromination is not a process of direct substitution, but is preceded by a reversible change of the acetone, accelerated by acids or alkalis, to a second form, probably the enol, this modification being brominated nearly instantaneously. It has already been shown that in many cases acids promote the attainment of equilibrium between *ketonic* and *enolic* modifications (*Trans.*, 1902, lxxxi., 1500, and *Proc.*, 1903, xix., 149).

The action of acids in accelerating substitution is not confined to aqueous solutions, but may be readily followed in other solvents.

The action of bromine and chlorine on other carbonyl compounds, as, for example, malonic ester and acetic anhydride, is greatly accelerated by acids. Even dry acetic acid is readily converted into its mono-bromo-derivative on the water-bath if it is first saturated with hydrogen chloride or bromide. The latter observation explains the action of a small quantity of phosphorus or phosphorus halogen compounds in promoting the action of chlorine and bromine on carboxylic acids, and the introduction of a suitable amount of the acid chloride appears equally effective when the acid contains water.

101. "*Reactions involving the Addition of Hydrogen Cyanide to Carbon Compounds.*" By A. Lapworth.

In order to ascertain the conditions under which hydrogen cyanide is most rapidly taken up by carbon compounds, camphorquinone was brought into contact with that substance in the presence of different agents which might possibly influence the reaction velocity, a rough measure of the latter being obtained by noting the speed with which the colour of the quinone disappeared.

The reaction, which was very slow in aqueous solution and was retarded by acids, was extremely rapid in presence of strong bases, and was accelerated by salts of weak acids. This result indicates that the change is effected by the cyanogen ions, a view confirmed by further experiments.

The great additive power of "nascent" hydrogen cyanide as compared with that of the agent in the free state is now readily understood, as the former occurs in presence of potassium cyanide.

When the addition product is fairly stable towards alkalis, it is not necessary actually to liberate the hydrogen cyanide. Camphorquinone may, in a few seconds, be largely converted into its cyanohydrin by shaking with a concentrated aqueous solution of potassium cyanide. Benzylidene benzylcyanide gives more than 30 per cent of the theoretical amount of diphenylsuccinonitrile if warmed for twenty minutes in alcoholic solution with excess of potassium cyanide, although it does not appear to unite with hydrogen cyanide in the absence of its salts; phorone is rapidly converted into phorononitrile under the same conditions.

With potassium cyanide, benzaldehyde yields mandelonitrile. The latter compound condenses with the former in presence of bases to yield hydrogen cyanide and benzoin. The well-known benzoin condensation may therefore be represented as the result of the formation of the unstable cyanohydrin of benzoin by the ordinary addition process,—

$$CHPh(OH)\cdot CN + PhCHO = OH\cdot CPh(CN)\cdot CHPh\cdot OH,$$

where the mandelonitrile behaves as the hydroxy-derivative of benzyl cyanide, a substance which is known to condense readily with benzaldehyde.

(To be continued).

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

The above Society met on Monday evening, June 22nd. Dr. C. E. Fawsitt in the Chair. Papers were read by Dr. Drinkwater and Dr. Hugh Marshall. There was a large attendance.

Dr. Drinkwater's paper was on "*Distillery Residues.*" He gave a description of the waste products produced in both grain and malt distilleries, and showed the manurial and feeding values of some of these products and their polluting effect when put into running streams. The vacuum methods which had been adopted during the last few years for dealing with these residues, and the results of experiments in filtering and treatment by septic tanks, were also discussed. He concluded by saying that he was in favour, on the whole, of evaporating the residue under suitable conditions, and using it as a manure.

The title of Dr. Marshall's paper was "*The Use of Carburetted Air for Lighting and other Purposes.*" In it he described and showed various lamps for burning carburetted air, prepared by passing ordinary air over blocks of absorbent material saturated with petrol or other highly volatile hydrocarbon mixtures. In some of these the supply of vapour to the burner is effected by gravity, but in others, more recently devised, the draught of the burner-tube draws the vapour from a carburetter placed below the burner proper. He also described improved arrangements for installation in country houses, by which a supply of carburettted air could be led over the house like an ordinary gas supply, and used for lighting, heating, &c.

NOTICES OF BOOKS.

An Index to the Complete Encyclopædia Britannica; being the Eleventh of the New Volumes which constitute in conjunction with the Existing Volumes of the Ninth Edition, the Tenth Edition of that Work. Vol. XXXV. of the Complete Work. Edinburgh and London: Adam and Charles Black; and *The Times*, Printing House Square. 1903. Pp. 1092.

With this volume we see the completion of the task undertaken by the Editors three and a-half years ago. The magnitude of such a work has necessarily taxed the energies of the Editorial Staff and their assistants to the utmost, but in spite of certain objections and protests that have been raised as to the somewhat strong American flavour of the work, there can be no denying the fact that this edition of the Encyclopædia Britannica reflects the highest credit on everyone concerned in its production.

It is hardly to be expected that special subjects, such as chemistry, physics, electricity, and the cognate sciences, could be dealt with in the same thorough manner as in the literature devoted entirely to these matters: still, although the space allotted to Science has been small in comparison with that devoted to other subjects, the materials have been supplied by the highest authorities in each special branch, and to the casual reader, whose interest is not that of a student, the articles will be found interesting and sound so far as they go. The great bulk of this work will prevent its acquisition by the small householder, but by the general public who can avail themselves of the numerous Public Libraries now springing up with such vigour all over the country, it will be found useful as a book of reference on practically every subject under the sun.

Fermentation Organisms; a Laboratory Handbook. By Alb. Klöcker. Translated from the German by G. E. Allan, B.Sc., and J. H. Millar, F.I.C., and Revised by the Author. With 146 Illustrations in the Text. London, New York, and Bombay: Longmans, Green, and Co. 1903. Pp. 392.

Although there are many books dealing with the micro-organisms of disease, it must be admitted that we have not been well supplied with works dealing with microbiology from the opposite point of view, viz., the micro-organisms which are serviceable or even necessary to man, and this is especially the case with regard to the more modern developments connected with the study of these organisms. It is for this reason that we welcome the publication of the present volume, which deals most thoroughly with the subject of fermentation organisms.

The book is divided into three sections, the first of which is introductory and covers a few pages only.

Section II. is on "The Laboratory," and deals in a minute and comprehensive manner with all the latest apparatus and instruments for the proper fitting-up of a modern bacteriological laboratory. It is assumed, of course, that the reader is not a beginner, but has already acquired some familiarity with bacteriological methods. But it should not be overlooked that though the broad principles of manipulative bacteriology do not vary, every writer has his own special methods, and many a useful dodge can be picked up from new publications.

In a subject such as the present one, where the preparation of pure cultures is so important, too great stress cannot be laid on the necessity for guarding against the intrusion of foreign germs. The precautions to be taken, and the various methods of sterilisation and culture, are all fully dealt with in this section.

Section III. deals with the micro-organisms of most importance in the fermentation industry; these organisms are, of course, partly useful and partly disadvantageous to the alcohol industry. They are all members of that branch of the plant kingdom called fungi, and here we find a review of the systematic connection of the micro-organisms to be described.

Yeast, which is the most important organism in connection with the brewing industry, belongs to the genus "Saccharomyces"; these are divided again into six species, according to which of the sugars, maltose, dextrose, lactose, saccharose, &c., they do or do not ferment. The systematic study of these organisms covers a good many pages. In this section we find also the inimical or disease organisms of fermentation; they are all treated in the same systematic manner as the others. It is not easy, in the compass of a short review, to give an adequate idea of the scope of this volume, nor of the care with which it has been prepared. We look upon it as a valuable contribution to the literature of micro-organisms, and feel sure that it will be read with both pleasure and profit, not only by the younger students, but by those who have already given much time and attention to this important subject.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Band III. 12 Heft. Edited by Franz Hofmeister. Braunschweig: Friedrich Viewig und Sohn. 1903.

The April number of this journal brings to a conclusion the third volume, and contains the index to the papers which have appeared in it. This number contains only three articles; the most important from a chemical point of view being, perhaps, the third, on the autolysis of the lymph glands. The author of this paper, A. Reh, has proved the formation of ammonia, leucin, tyrosin, thymin, and uracil; thus partly confirming results which have been previously obtained by other investigators, and also adding to them, as in the case of uracil, which has not been detected before, among the products of the autolysis of the lymph glands. In the long paper on the coagulation of the albuminous substances of muscle, and their supposed connection with muscle rigor, a particularly exhaustive research into the subject is described, with the details and results of many experiments.

Die Aluminium-Industrie. ("The Aluminium Industry"). By Dr. F. Winteler. Braunschweig: Friedrich Viewig und Sohn. 1903.

The author of this work, feeling that up to the present most of the books published on such subjects as the above have been too much occupied with the repetition of lists of patents, has endeavoured to produce a convenient work for the use of students and technical men, who require more information on the actual methods and processes employed than on the details of the advance of our knowledge of the more purely scientific aspect of the subject. Thus he has excluded all that is useless from a practical point of view, and aimed at supplying the want of the means of obtaining trustworthy details as regards the preparation, &c., of aluminium on a large scale in a convenient form. The result is eminently satisfactory, and the book fulfils its purpose admirably. The properties of

the metal, both physical and chemical, are given in full, and modern methods of analysis are included in a section, which, though succinct, is quite sufficiently detailed. The book concludes with the description of the applications and uses of aluminium, and the preparation and properties of some of its alloys.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 22, June 2, 1903.

Cementation of Steels.—Léon Guillet.—The author's researches on the cementation of steel show—(1) That the rapidity of penetration of carbon into the steel depends on the temperature, the time, and the chemical reactions produced by the carbon; (2) the experiments made did not determine the solubility of the carbon in the iron, but they apparently establish the fact that there is a preliminary state of equilibrium which is destroyed by the final operation; (3) by simple cementation certain steels containing nickel acquire the same hardness as carbon steels.

The Form in which Mercuric Iodide goes into Solution.—D. Grenez.—The author shows that the vapours emitted by red quadratic mercuric iodide at temperatures below the transformation-point (126° under atmospheric pressure) take the yellow orthorhombic form on condensation. He further investigates the form in which mercuric iodide goes into solution, and comes to the conclusion that the two changes of state of red mercuric iodide, either when volatilised or when dissolved, cause the body to be transformed into the unstable yellow variety, even when the transformation takes place at temperatures at which the red iodide is in its most stable state.

Precipitation of Manganese by Persulphuric Acid in Acid Solution.—H. Baubigny.—This paper gives an account of the further researches by the author on the precipitation of manganese by persulphuric acid, when various changes take place in the relative acidity of the solution and of the absolute mass of free H_2SO_4 as compared with the weight of the manganese.

Alloys of Copper and of Magnesium.—O. Boudouard.—The author investigates the relation between the fusibility and the physical and mechanical properties of the alloys of copper and magnesium. The curve of fusibility shows the existence of three definite compounds—Cu_2Mg, CuMg, and $CuMg_2$. Constants obtained by microscopic metallography and chemical analysis confirm the existence of these definite compounds.

Chromium Silicides.—P. Lebeau and J. Figueras.—The action of silicon on a metal in presence of copper allows of the preparation of the definite compounds which silicon forms with iron, cobalt, and manganese. The method consists in reacting on a mixture of copper and of the metal with varying proportions of silicon in the form of siliciuretted copper, free silicon, or silicon obtained from the action of sodium on an alkaline fluosilicate. By applying these methods to the binary combinations of chromium and silicon, the authors succeed in isolating the four chromium silicides, $SiCr_3$, $SiCr_2$, Si_2Cr_3, Si_2Cr.

Electrolytic Reduction of Incomplete Acids.—C. Marie.—The author's researches on the electrolytic reduction of incomplete acids show that the double ethylenic liaison is capable of fixing a hydrogen atom during electrolysis. In the case of bodies which are easily oxidised this property prevents their electro-chemical oxidation; it also prevents the necessity of the preparation and somewhat difficult application of sodium amalgam.

Dibromo-acetylene, $CBr{\equiv}CBr$.—P. Lemoult.—The author succeeds in preparing dibromo-acetylene and identifying it by certain characteristic properties. The principle of the preparation consists in transforming two molecules of HBr into symmetric tetrabromethane, $CHBr_2$—$CHBr_2$. This transformation is attended by many difficulties, because the body obtained is spontaneously inflammable in air, is decomposed by heat, and is explosive. It is a colourless liquid of density 2; it is incapable of being distilled without decomposition even *in vacuo*; its boiling-point is about 80°; and it is soluble in the majority of organic solvents.

MISCELLANEOUS.

On Terbium.—R. Marc.—Oxide of terbium has a very marked brown ochre colouration. That which has been described previously was nothing better than a mixture of yttria with other heavier earths, which were colourless, and had no absorption spectrum (ytterbium, no doubt), and were coloured by a little terbium. Terbium has two degrees of oxidation; a lower, coloured oxide, and a colourless peroxide (as with praseodymium). Its absorption spectrum appears to be characterised by a band, $\lambda = 464$—461. Its atomic weight is about 157.—*Berichte*, vol. xxxv., p. 2382.

Soluble Salts of Manganese.—Recent experiments have afforded increased evidence that manganese possesses useful qualities in the treatment of debilitating diseases associated with anæmia. It appears, however, that the nature of the combination in which the manganese is employed exercises an important influence upon the therapeutic effects. Some experiments conducted in the Wellcome Chemical Research Laboratories, with a view of preparing a soluble salt of manganese of a stable character, have proved highly satisfactory. As a result of these investigations Messrs. Burroughs, Wellcome, and Co. are manufacturing a soluble citrate of manganese, as well as two soluble compounds of manganese and iron.

The Determination of the Principal Impurities in Anthracene.—H. Behrens.—For the detection of carbazol in anthracene the latter is exhausted with acetic ether; the solvent is allowed to evaporate, and the residue taken up again with a few drops of the same liquid; after evaporation on a watch-glass a residue is obtained, of which the centre consists of anthracene and the periphery of carbazol. A little of this latter substance is dissolved in a drop of nitrobenzene treated with a little phenanthrenequinone; the presence of carbazol causes the appearance of copper-coloured tablets. In the case of phenanthrene, we substitute benzene for the acetic ether, and the characterisation is done by means of *a*-dinitrophenanthrenequinone in nitrobenzene.—*R. Tr. Ch. P.-B.*, No. 2 and 3, p. 252.

Thallous Sulphates.—W. Stortenbeker.—The presence of 1 to 2 molecules of H_2SO_4 for each one of Tl_2SO_4 dissolved in water helps the crystallisation; much larger crystals are obtained. One molecule of Tl_2SO_4 is soluble at 18° in 600 molecules of water, and, on the other hand, in 193 molecules of water treated with 9·4 molecules of H_2SO_4; this latter solution, after being concentrated down to one-half, deposits an *acid sulphate of thallium*, $(SO_4)_2Tl_3H$, or SO_4Tl_2,SO_4HTl, in pearly hexagonal flakes. By concentrating the acid solution of SO_4Tl_2 strongly on the water-bath, the author obtained the *acid sulphate*, SO_4HTl, in square hygroscopic plates, fusible at 115—120°; this salt appears to be dimorphous; in fact, we find prismatic orthorhombic needles, along with these clinorhombic plates.—*R. Tr. Ch. P.-B.*, vol. xxi., No. 1, p. 87.

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2276.

ON THE ATOMIC WEIGHT OF LANTHANUM.

By HARRY C. JONES.

In a recently described determination of the atomic weight of lanthanum, Brauner and Pavlicek (*Amer. Chem. Journ.*, 1902, xxviii., 23) found the value 139·04. A careful examination of their paper shows that a large amount of painstaking work was done, and great care was exercised in certain directions. Their value, however, differed from my own by a little more than a quarter of a unit (*Journ. Chem. Soc.*, lxxxi., 1243).

It was obvious, therefore, that there must be some hidden source of error in at least one of the series of determinations, and possibly in both.

Work was undertaken with the object of determining, if possible, the cause of the difference between the values found by Brauner and those obtained in this laboratory.

An examination of the paper by Brauner and Pavlicek, which was not published in full until after the appearance of my own, convinced me that, notwithstanding the fact that they had undoubtedly taken very great care in certain directions, in other directions their work contained possible sources of error. Their own rather sweeping criticism of a large number of investigations by careful workers, near the close of their paper, viz., "*all atomic weight determinations of the rare earth elements made by the synthetical sulphate method during the nineteenth century are vitiated by an error which tends to lower the atomic weight and diminishes as the basicity of the earth decreases*," seemed to me not to be sufficiently substantiated by experiment. This would probably depend upon the *temperature* to which the sulphate had been heatad, and also the *time* during which it was heated, free access of air, &c. This point was very carefully tested in my earlier work, using methyl orange as the indicator, and *not the slightest trace of acidity* could be detected.

Quite recently a criticism of my work by Brauner has appeared, in which a number of points are raised (*Zeit. Anorg. Chem.*, 1903, xxxiii., 317). He thinks that my material was not sufficiently free from cerium, after I had stated that "The oxalate was then decomposed to the oxide and analysed spectroscopically by Mr. L. E. Jewell, whose work in this field is so well known. The only impurity which could be detected was a trace of cerium, and this was not more and probably much less than 0·01 of 1 per cent." This analysis was made by means of the large Rowland spectroscope, by one of the most expert spectroscopists living, and I therefore think the results can be accepted, notwithstanding Brauner's opinion to the contrary. A moment's thought would, however, convince any one that traces of cerium would produce a negligible influence, since the atomic weight of cerium is so close to that of lanthanum.

Brauner's suspicion that in my determinations some of the oxide was lost by spattering, would have been removed by carefully reading what was stated on this point.

The various other points referred to by Brauner are matters which would be looked after and guarded against by any one in an ordinarily careful quantitative analysis, and still more, of course, in an atomic weight determination, and there seemed to be no occasion on my part to refer to them in print.

Possible Sources of Error in the Work of Brauner.

I was particularly impressed in reading the paper by Brauner and Pavlicek with the fact that they heated the oxide of lanthanum in a platinum crucible placed inside another platinum crucible. They themselves state that the oxide in "contact with the hot walls of the platinum crucible assumed an extremely slight pale buff tint. This tint was slightly more prominent in the higher fractions."

In my own work, I at first had used this same method for heating the oxide to constant weight. I had also observed that the oxide next to the platinum became coloured, and immediately abandoned the platinum crucibles altogether, and adopted porcelain crucibles in their stead. I supposed that the change in colour indicated a change in the composition of the oxide—a supposition which we shall see later is made highly probable.

Brauner determined the amount of acid sulphate in his product by titration with a standard alkali, and introduced the corresponding correction. It is difficult to see how he knew the *composition* of the acid sulphate which was present in such very small quantities. This, of course, could not be assumed from the composition of the acid sulphate prepared under different conditions.

One reads Brauner's paper in vain for an account of a thorough *spectroscopic* study of the material which he used in his work. This does not refer to a study of the absorption spectrum, since many substances do not yield characteristic absorption spectra, but to a careful examination of the emission spectrum. Certainly no material should be used to-day for atomic weight work, whose emission spectrum had not been carefully photographed, and the proper comparisons made to determine the presence or absence of foreign substances. This is especially desirable in the case of the rare earths, where, on account of the unusual similarity in the chemical properties of the substances, chemical methods are not capable of detecting traces of impurities, if these impurities are the other rare earths. I do not doubt that the Rowland spectroscope would have convinced Brauner that his lanthanum contained at least traces of impurities, and that he was not dealing with absolutely pure material.

One other point in connection with the work of Brauner and Pavlicek seems to call for special comment. They state (*Journ. Chem. Soc.*, 1902, lxxxi., 1252): "On heating the salt (lanthanum sulphate) to a temperature which in some cases may have finally exceeded 600°, that part which adheres to the platinum walls of the crucible may become partly converted into the *basic* salt, that part which lies nearer the centre may consist of the *normal* salt, and the uppermost inner layer may consist of some incompletely decomposed *acid* sulphate."

This would show that the sulphate was not heated uniformly throughout; the outer layer being heated to the highest temperature, the middle layer less highly heated, while the innermost layer was still less strongly heated. This is quite explicable when we consider the arrangement used by Brauner and Pavlicek for heating the sulphate. They state (*Journ. Chem. Soc.*, 1902, lxxxi., 1250) that "the platinum crucible was fastened in the centre of a large porcelain crucible, having in its lid a thermometer graduated up to 550°, by which, at least, the order of the temperature was indicated. The large crucible fitted into a larger plate of asbestos cardboard, in order to exclude the products of the combustion of coal."

Under the above conditions, with such a small air-space around the platinum crucible, it is obvious that the sulphate would be heated to a temperature which grew less and less as the distance from the platinum walls increased, and the temperature indicated by the thermometer suspended in the air in the innermost crucible may have borne no very close relation to the temperature of the lanthanum sulphate in contact with the platinum. The thermometer would, obviously, have indicated a considerably lower temperature than that to which the outer layer of lanthanum sulphate was subjected, and have given no clue to the correct temperature of the sulphate in contact with the platinum. This is shown by the fact that the outer layer of sulphate was partly decomposed into basic sulphate, while the inner layer still contained some acid sulphate,

Some New Determinations of the Atomic Weight of Lanthanum.

I determined to repeat my earlier work on the atomic weight of lanthanum, taking even greater precautions in heating the substances and preserving them in the dry condition until weighed. It was thought that in the repetition of the work possibly some sources of error might appear which had been overlooked. The oxide was highly heated over the blast-lamp in a porcelain crucible, and was *perfectly white*. It was transferred red-hot to a desiccator containing fresh phosphorus pentoxide, and allowed to cool over the pentoxide. It was finally weighed in the platinum crucible in which the determination was to be made, the platinum crucible and oxide being enclosed in a ground-glass stoppered weighed tube. The remaining operations in connection with the synthesis of the sulphate were essentially the same as in the first series of determinations. The sulphate was always weighed in the platinum crucible, which was placed, while hot, in a ground-glass stoppered weighing tube, and the whole allowed to cool in a desiccator over fresh phosphorus pentoxide. Special care was taken to test for the presence of acid sulphate, using methyl orange. A given number of drops of the indicator was added to the solution of lanthanum sulphate, and an equal number to an equal volume of pure, re-distilled water. The water used to dissolve the lanthanum sulphate, and for comparison, had been distilled from chromic acid and then from barium hydroxide, and had a conductivity of $1{\cdot}2 \times 10^{-6}$.

The two tubes—the one containing the lanthanum sulphate and the indicator, and the other the pure water and the indicator, were then passed around the laboratory to the several instructors and advanced workers, with the request for them to decide which solution showed an acid reaction. In no case could any difference by detected by any one.

The question of the solubility of the lanthanum sulphate in pure water was then carefully tested in each experiment. The sulphate dissolved *at once*, on coming in contact with the water, and manifested none of the behaviour described by Brauner and Pavlicek (*Journ. Chem. Soc.*, 1902, lxxxi., 1252). This convinced me that Brauner and Pavlicek were justified in concluding that their sulphate was not homogeneous, and that the cause of the heterogeneity of their material was, as already suggested, that the sulphate was heated in an air-bath which was too small to permit of a uniform heating of the salt.

Results.

The results of five determinations are given below :—

	La_2O_3.	$La_2(SO_4)_3$.	$3SO_3=240{\cdot}18$.	At. wt. La.
I.	1·2161	2·1132	0·8971	138·79
II.	1·6311	2·8342	1·2031	138·81
III.	1·7804	3·0938	1·3134	138·79
IV.	1·4168	2·4619	1·0451	138·80
V.	1·9702	3·4235	1·4533	138·80

Average = 138·80

The average of these results, 138·80, differs from the mean of my first ten determinations—138·77—by an amount not larger than the possible experimental error (*Amer. Chem. Journ.*, 1902, xxviii., 33).

Determination of the Atomic Weight of Lanthanum when the Oxide is Heated in Platinum.

Having found essentially the same value for the atomic weight of lanthanum in this series of determinations as in the earlier series, it occurred to me to make a determination or two, heating the oxide in one platinum crucible placed inside of another platinum crucible, as Brauner had done. The two platinum crucibles were separated by a small piece of asbestos paper to avoid any tendency for them to stick together when heated over the blast-lamp. In the first of the following determinations the oxide was heated for *two hours* in platinum. Although the oxide remained *perfectly white* when heated in porcelain for any length of time, when heated in platinum in the manner above described, it showed a marked tint, especially next to the walls of the platinum where it had been most highly heated.

In the second determination, recorded below, the oxide was heated in the platinum crucible for *five hours*, and showed *deeper coloration* than the oxide that had been heated a shorter time.

	La_2O_3.	$La_2(SO_4)_3$.	$3SO_3=240{\cdot}18$.	At. wt. La.
I.	1·2820	2·2264	0·9444	139·02
II.	1·3885	2·4110	1·0225	139·08

The results thus obtained are not only higher than those found in my work, but differ appreciably as the time during which the oxide of lanthanum was heated in the platinum was increased.

The higher value found would indicate that the lanthanum oxide had undergone slight oxidation in the platinum. This was tested by transferring the oxide which had been heated in platinum for several hours to a porcelain boat, inserting the boat into a large tube of hard glass through which a current of hydrogen was passed, and heating the tube on a combustion furnace. *The oxide, under these conditions, lost in weight.* A loss as great as 0·002 grm. per grm. of oxide was detected when the oxide was heated in a current of hydrogen for from one to two hours.

In the very first stages of my work on the atomic weight or lanthanum, I heated the *perfectly white* oxide, obtained by decomposing the oxalate and heating the resulting oxide in porcelain, in a current of hydrogen to a bright-red heat for two hours, without being able to detect the slightest loss in weight. It is, of course, absolutely essential in this work that under the above conditions there should be no loss in the weight of the oxide, otherwise it would be very probable that we were dealing with the sesquioxide containing a small amount of a higher oxide of lanthanum.

In my opinion, the above facts account satisfactorily for the difference between Brauner's result and my own. If Brauner will heat his oxide only in porcelain, and not in platinum, he will obtain a lower value for the atomic weight of lanthanum. In reference to the atomic weight of praseodymium it is almost superfluous to repeat what has already been said. The question of the presence of both *acid* and *basic* salts was carefully considered (*Amer. Chem. Journ.*, 1898, xx., 353), and the result recorded five years ago. Notwithstanding this fact, Brauner and Pavlicek (*Journ. Chem. Soc.*, 1902, lxxxi., 1249) state that :—"No one, however, has considered the other side of the question, How can we find out whether the sulphate does not contain an *excess* of sulphuric acid?" The mean of my results, 140·46, agreed so well with that found simultaneously by von Scheele (*Zeit. Anorg. Chem.*, 1898, xvii., 310), working with Clève, 140·40, that further work along this line seemed superfluous to both von Scheele (*Ibid.*, 1901, xxvii., 57) and myself. This was especially the case when we considered that the two pieces of work were done with entirely different material, obtained from very different sources, purified in different ways, and the determinations, although carried out by essentially the same method, must have involved very different details in the manner of heating the oxide and sulphate. The temperatures to which these substances were heated in the two sets of determinations were probably quite different, and might have been very different.

When we consider all of these facts the agreement between the results of von Scheele and my own is really quite remarkable, and makes it highly probable that objections such as those urged by Brauner are untenable. If such objections were really valid it is almost inconceivable that they should have affected the two sets of determinations in exactly the same way and to exactly the same extent in every case.

Brauner's value for the atomic weight of praseodymium differs from that of von Scheele and my own by about one-half a unit. Brauner's value for the atomic weight of

neodymium in one series of determinations is nearly identical with my value. In another series it is about 0·2 of a unit higher. Unless these differences can be explained on the same ground as in the case of lanthanum, no satisfactory explanation has yet been furnished.

Johns Hopkins University,
April, 1903.

CYANOGENESIS IN PLANTS.*

Part III.—Phaseolunatin; the Cyanogenetic Glucoside of *Phaseolus lunatus*.

By WYNDHAM R. DUNSTAN, M.A., F.R.S.,
Director of the Imperial Institute, South Kensington,
and
T. A. HENRY, D.Sc., London.

Phaseolus lunatus is an annual plant probably indigenous to South America, but now generally cultivated throughout the tropics for the sake of its nearly white edible bean, often known as the "Lima" or "Duffin" bean. In Mauritius the plant is grown under partial cultivation for use as a green manure, and produces under these conditions beans which differ from those obtained under thorough cultivation, in exhibiting dark brown or purple seed coats, and in being more or less poisonous. The poisonous properties of these beans have been shown by M. Bonamé ("Rapport Annuel de la Station Agronomique de Mauritius," 1900, p. 94) to be due to the production of hydrocyanic acid, which is formed when the crushed beans are moistened with water. Subsequently van Romburgh (*Annales de la Jardin botanique de Buitenzorg*, Series II., vol. i., p. 2) verified this observation and showed that acetone was simultaneously formed.

In continuation of our investigation of the production of prussic acid by plants, we have further investigated this subject. The seeds of *Phaseolus lunatus*, collected in Mauritius through the kind offices of M. Bonamé, have been found to contain a cyanogenetic glucoside, which has been named phaseolunatin. This glucoside crystallises in colourless needles, is readily soluble in water, and is lævorotatory in solution. Its composition is expressed by the formula $C_{10}H_{17}O_6N$. When hydrolysed by emulsin or by boiling with dilute acids, it is converted into acetone, dextrose, and hydrocyanic acid, according to the equation—

$$\underset{\text{Phaseolunatin.}}{C_{10}H_{17}O_6N} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Acetone.}}{(CH_3)_2CO} + \underset{\text{Hydrocyanic acid.}}{HCN}.$$

When warmed with alkalis, phaseolunatin is converted by hydrolysis into phaseolunatinic acid, and this acid, by the further action of dilute acids, is decomposed into dextrose and α-hydroxy*iso*butyric acid. These two reactions are represented by the following equations—

$$\underset{\text{Phaseolunatin.}}{C_{10}H_{17}O_6N} + 2H_2O = \underset{\text{Phaseolunatinic acid.}}{C_{10}H_{18}O_8} + \underset{\text{Ammonia.}}{NH_3}.$$

$$\underset{\text{Phaseolunatinic acid.}}{C_{10}H_{18}O_8} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{α-Hydroxy\textit{iso}butyric acid.}}{C_3H_6(OH)COOH}.$$

These observations prove that phaseolunatin is the dextrose ether of acetonecyanhydrin, and that its constitution is represented by the formula—

$$(CH_3)_2C(CN)—O—C_6H_{11}O_5.$$

Phaseolunatin is, therefore, the first member of a new class of natural cyanogenetic glucosides since it contains an aliphatic nucleus; amygdalin, dhurrin, and lotusin, the other known cyanogenetic glucosides, being aromatic compounds.

* Abstract of a Paper read before the Royal Society, June 5, 1903.

The enzyme present in the seeds of *Phaseolus lunatus* has been examined and shown to be identical in its properties and in the effects it produces with the emulsin of almonds.

Specimens of the so-called "Rangoon" or "Paigya" beans derived from *Phaseolus lunatus*, grown in India and imported into this country for the manufacture of cattle food, have also been examined and shown to contain a small quantity of phaseolunatin. The amount of hydrocyanic acid producible from the seeds of *Phaseolus lunatus* has been found to vary from 0·041 per cent in the case of light brown beans, to 0·088 per cent in the case of dark brown or purple beans. The specimens of "Rangoon" beans examined furnished on an average about 0·004 per cent of this acid.

The authors draw attention to the fact that under cultivation this plant furnishes light coloured or white beans, which are incapable of producing prussic acid, and contain no phaseolunatin, although the enzyme emulsin is still present. In this respect the seeds of *Phaseolus lunatus* resemble those produced by the two varieties of almond (*Prunus amygdalus*). The bitter almond contains both the cyanogenetic glucoside, amygdalin and the enzyme emulsin, while the sweet almond contains emulsin only.

Treub (*Annales de la Jardin botanique de Buitenzorg*, 1895, vol. xiii., p. 1) has suggested that in the case of *Pangium edule*, the at present unknown precursor of prussic acid in this plant may play the part of a formative material in the synthesis of amides and proteids. This is also probably true of the cyanogenetic glucosides which the authors have isolated from *Lotus arabicus*, *Sorghum vulgare*, and *Phaseolus lunatus*. The absence of phaseolunatin from the seeds of the cultivated *Phaseolus lunatus* and of amygdalin from those of the sweet almond, which there is reason to believe is the cultivated variety of *Prunus amygdalus*, may be the result of the more active metabolism induced by improved nutrition and environment, which leads to the more rapid utilisation of the glucosides by the cultivated plant, so that no supply of these substances is available for storage as reserve materials in the seeds.

EXPERIMENTAL DETERMINATION OF EQUIVALENTS.

By JOHN BRIDGEFORD COPPOCK, F.I.C., F.C.S.

This method consists in using the inner tube of a Lothar Meyer's vapour-density apparatus. It lends itself to a lecture table method of determining the equivalents and illustrating respectively the mono-, di-, and trivalency of sodium, magnesium, and aluminium. The apparatus is fitted up as for a vapour-density determination, with the omission of the outer tube.

Method.

For Sodium.—Use a small weighing bottle or corked test-tube. Quickly cut and dry a small piece of sodium, introduce it into the weighing vessel, and weigh again. This weighed quantity of sodium is allowed to fall down the experimental tube into methylated spirits or a mixture of alcohol and water. The hydrogen is slowly evolved, and is collected in the graduated gas tube.

For Magnesium.—A small piece of bright metal, after weighing, is dropped down the experimental tube into dilute hydrochloric acid. If commercial magnesium be used the amount of carbon in it will introduce an error.

For Aluminium.—Commercial aluminium may be used. A small quantity is weighed out and dropped into strong hydrochloric acid in the experimental tube. Acid in the proportion of ten volumes of acid to one of water is a convenient strength.

Results.

Weight of metal introduced.	Volume of hydrogen liberated at 10° C. and 750 m.m.	Corrected volume.	Equivalent found.	Standard equivalent.
Grm.	C.c.	C.c.		
		Sodium.		
0·078	39·4	37·5	23·21	23
0·074	37·2	35·4	23·32	23
		Magnesium.		
0·0505	48·2	45·88	12·28	12·15
0·0457	43·7	41·66	12·26	12·15
		Aluminium.		
0·0326	42·5	40·46	8·99	9·03
0·0350	45·4	43·22	9·04	9·03

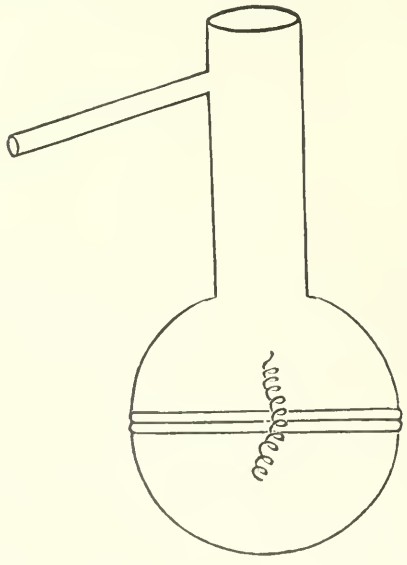
Science Schools, Stroud, Glos.

AN IMPROVED DISTILLATION FLASK.

By JOHN McDONALD.

After the organic chemist has extracted with ether, benzene, &c., he has often to recover the solvent by distillation, and if the substance extracted is a solid it is a matter of some difficulty to get it out of the flask. To overcome this difficulty I have made the following modification.

The flask is made in two parts, which are ground together. The inner edge of bottom half has six small studs of glass projecting up about one-eighth of an inch above the rim, and the upper part just fits over those studs, and has its ground edge fitting on to the ground edge of the under half. The studs are to prevent the two halves from slipping off each other.



The flask is held together by three spiral springs fixed on to three glass hooks placed at equal distance to each other on the upper and under part, and the tension of those springs entirely prevents leaking.

After distilling the two halves are separated by loosening the springs, and the substance can then be conveniently scraped out with a spatula.

The accompanying figure will make the description clear.

METEORIC DUSTS, NEW SOUTH WALES.*

By Prof. A. LIVERSIDGE, LL.D., F.R.S., University of Sydney.

Introductory.—The term meteoric dust is used because it is commonly applied to the materials forming the subject of this paper; it is not, however, intended to state that the dusts are necessarily wholly of cosmic or extra terrestrial origin. The specimens described and exhibited were from Moruya (fell on Dec. 15th, 1880), from Uralla (fell on Dec. 14th, 1882), from near Broken Hill (fell 1896)), from Menindie (fell June 17th, 1899), and Pambula (fell Oct. 5th, 1899). Dust from the roof-beams and mud from a covered cistern at the University, and from the roof of the Observatory, Sydney, were collected in 1882.

All the dusts are of a reddish colour except those from the University and Observatory, which are grey. The red dusts are mainly siliceous and argillaceous, and look as if they had come from dried-up water-holes; they contain a variety of organic and mineral matters such as might be expected from such sources, and in addition magnetite and metallic iron, containing cobalt and nickel.

The University and Observatory dusts also yielded magnetite and metallic iron containing cobalt and nickel.

Meteoric Dust, Moruya, N.S. Wales.—The specimen of meteoric dust forming the subject of this note was forwarded to me by Mr. H. C. Russell, Government Astronomer, who informs me that it fell on December 15th, 1880, at Moruya, a small town in New South Wales, 198 miles south of Sydney and distant 5 miles from the sea.

The specimen consists of a pale clay- or snuff-coloured powder, of uniform tint and appearance; for the most part it is composed of an impalpable dust, but on carefully flattening it out under a spatula and on rubbing it between the finger and thumb a few coarser gritty particles can be felt. To separate the finer material from the coarser particles, a portion of the dust was placed in a tall conical precipitating glass, and subjected to the action of a stream of water carried down by means of a glass tube to the narrow bottom of the glass. The residue left in the glass was found to be made up of grains of quartzose sand and white particles, the latter dissolving readily in dilute acids with effervescence; some of these were grains of amorphous calcium carbonate, but a few of the larger were readily recognised under the microscope as fragments of shells, but whether of fresh-water or marine mollusca could not be decided, as they are much abraded; in addition there are some rather larger soft black particles which readily flatten out under the spatula to an unctuous black mass; when ignited on platinum-foil these black particles slowly burn away with but slight incandescence, like charcoal, but emit a strong empyreumatic odour, and leave a bulky white ash; some of them when crushed and examined under the microscope present a cellular structure very similar to that of wood, but rather obscure; others, however, are devoid of all recognisable structure.

The more or less complete obliteration of the original structure is due to the fact that the wood has undergone considerable change, either by natural decay or by the effects of fire. The woody matter does not, however, present the appearance of ordinary charcoal, such as might have been recently derived from house or bush fires; it has evidently been long subjected to the action of water, and it is highly probable that some of it is not charcoal but simply fragments of water-logged woody matter, black from decay, common in rivers and fresh-water lakes and ponds. Intermixed with the other substances there is also a certain proportion of less decomposed vegetable matter in a flocculent state, and the remains of two or three small beetles were present—all such substances were removed as completely as possible before making the chemical examination; some minute particles of a yellowish mica are

* Read before the Royal Society of N.S. Wales, September 3, 1902. From the *Journal and Proceedings of the Royal Society of N.S. Wales*, vol. xxxvi., p. 241.

scattered through the specimen ; mica is common in many muds, especially in those deposited by water running over granite, gneiss, or similar rocks ; the rock about Moruya is granite, hence the presence of the mica can be accounted for locally.

As it was thought that particles of metallic iron might be present, a magnet covered with a movable paper cap was repeatedly drawn through the powder, when a few scaly fragments of the metal with jagged edges were obtained—the fragments were found to be malleable, but not highly so, since they rather readily split up under the pestle when crushed in an agate mortar ; they also became burnished, and acquire the usual colour and metallic lustre of iron. They at once reduce a solution of sulphate of copper and become coated with metallic copper, apparently just as readily as ordinary iron ; they also afford the usual reactions for iron on the application of the wet tests ; cobalt is present in sufficient proportion to give the usual blue colour with the borax bead, and I believe that nickel is also present, but the quantity of metal was not sufficient to satisfactorily determine this, neither did it afford conclusive evidence as to the presence of sulphur and phosphorus.

The total quantity of magnetic matter separable by the magnet out of 27·524 grms. of the dust (the whole of that at my disposal) amounted to but 0·009 grm. ; the largest fragment weighed 0·0019 grm.

Externally the iron particles are covered with a thin coating of ordinary red rust, the hydrated sesquioxide of iron, and present no traces of fusion nor of the skin of magnetic oxide, usually present on the surface of large masses of meteoric iron.

The minute fused or round globules of iron met with by Mr. Murray (now Sir John Murray, K.C.B.) in the dredgings obtained by H.M.S. Exploring Vessel *Challenger*, were specially sought for, but without success (*Proc. Roy. Soc. Edinburgh*, 1876, 258).

On heating the dust in a glass tube it readily blackens, gives off water with a strongly marked alkaline reaction, and emits an empyreumatic odour ; hence there is a notable proportion of nitrogenous organic matter present, and this is confirmed by its behaviour when heated on platinum-foil, for it at once blackens, and the scattered particles of organic matter ignite, and are seen as glowing points or sparks running over its surface ; at the same time, a well marked nitrogenous odour is evolved. After burning off the whole of the combustible matter the residue is of a reddish clay-brown colour not materially different from that of the original substance. Apart from the larger woody particles, the organic matter must be very uniformly distributed, since the dust appears on ignition to blacken equally throughout.

Under the microscope the dust is seen to be almost entirely composed of small particles between 1/2000th and the 1/500th of an inch in diameter, or 0·01 to 0·02 m.m., a few of the coarser grains of sand being about 1/25th of an inch, or 1 m.m. Very few of them are quite opaque, the larger grains are colourless and transparent, but most of the smaller particles transmit a yellowish-brown colour ; with but very few exceptions the particles are rounded or sub-angular, as if wind or water worn, and with no recognisable traces of igneous fusion. Some diatom frustules are sparingly scattered through the dust ; these strongly resemble, and may be identical with, *Diatoma vulgare* and *Surirella constricta* ; a few siliceous spicules, something like sponge spicules, are also present ; these together with the diatoms are rather more readily detected after treating the dust with nitric acid. A few vegetable fibres, including some filaments of cotton, together with vegetable spores, are also revealed by the microscope. There are also a few scattered minute black non-magnetic particles which are probably chrome-iron, but the quantity is insufficient for me to satisfy myself on this point.

A qualitative examination yielded me the following results :—The presence of organic matter, water both hygroscopic and combined, silica both as free quartz and in combination with bases, mainly with alumina in the form of clay ; iron, metallic, and in combination as oxide, cobalt, and probably nickel, a trace of copper, manganese, lime, magnesia, potash, soda, and small quantities of hydrochloric, sulphuric, phosphoric, and carbonic acids. The dust appears to consist mainly of finely divided clay mixed with other substances.

The hydrochloric acid, as soluble chlorides, is present in rather greater quantity than either the sulphuric or carbonic acids ; there is but a trace of phosphoric acid.

An examination with the spectroscope failed to reveal the presence of any rare or unusual element in either the soluble or insoluble portion.

A quantitative examination gave the following results :—

Moisture at 100°	5·400
Loss on ignition	9·700
Silica	58·020
Alumina	17·184
Ferrous oxide	1·214
Ferric oxide	4·237
Lime	2·270
Soda	traces
Potash	trace
Undetermined	1·975
	100·000

As the result of the examination, I think that part of the dust is of meteoric origin, but there is also no doubt that the main bulk of it is from terrestrial sources. I do not think it is of volcanic origin, since it does not present the characters of a volcanic ash ; there are but few traces of augite or other crystals such as we might reasonably expect to be present in a wind-borne volcanic dust ; further the large proportion of combustible matter present is against this idea. Most of it has doubtless been derived from the deposits left by dried-up fresh water pools, lakes, or water-courses, for with the exception of the fragments of shells, the dust is quite unlike a sea-shore deposit ; the shells and diatoms may be either of fresh-water or marine origin, the sponge spicules, however, point to the latter source, but these together with other portions of the dust may not have been deposited at the same time. More light would probably be thrown upon the question could specimens of the mud which fell at the same time on board ships off the coast be submitted to an examination.

I do not suppose that much if any of the combustible matter is of meteoric origin, although considerable amounts of carbonaceous and bituminous substances have been met with in several meteorites, *e.g.*, the Bokkeveld, Kaba, and other meteorites ; the nickel-iron meteorites found at Bingera, N.S.W., and elsewhere, contain carbon ; in fact, carbon is commonly present in metallic meteorites. But I think the metallic portion is of meteoric origin and perhaps part of the earthy matter also. The probability of the metallic portion being of cosmic or meteoric origin is borne out by the peculiar appearance of the iron, its imperfect malleability, resembling in these respects certain other irons of undoubted meteoric origin ; by the presence of cobalt and the probable presence of nickel ; copper was found in the hydrochloric acid solution of the dust, and it may or may not have been present in the metallic iron also ; the quantity of metal extracted by the magnet and separately examined was too minute to determine this. Copper has been detected in many meteorites, and in several specimens of meteoric dust, and it was found, together with metallic iron, cobalt, and nickel, by Mr. J. Y. Buchanan, M.A., F.R.S., chemist and physicist to the *Challenger* expedition, in the clays, manganese nodules, and cosmic dust which were dredged up (*Proc. Roy. Soc.*, 1876, p. 531).

A specimen of dust which fell on board a ship in the Atlantic was found by Gibbs to contain copper ; after driving off 18·53 per cent of water the composition was found to be as follows :—

Silica	45·58
Alumina	20·55
Ferric oxide	9·39
Manganic oxide	4·22
Calcic carbonate	11·77
Magnesia	2·21
Potash	3·64
Soda	2·33
Cupric oxide	0·31
	100·00 (*a*)

(*a*) Watts's "Dictionary of Chemistry," vol. iii., p. 982.

M. G. Tissander (*Comptes Rendus*, lxxxiii., p. 821) states that he found the dust which he collected from one of the towers of Notre Dame in Paris, into which no one had entered for years, to closely resemble that which he detached by friction from meteorites. He found metallic iron, probably of extra-terrestrial origin, in all the samples examined. An analysis of one gave him the following results :—

Dust from the Tower of Notre Dame.

Organic matter rich in carbon	32·265
Soluble in water, chlorides, and sulphates of the alkalis and alkaline earths, ammonium nitrate	9·220
Iron sesquioxide	6·120
Calcium carbonate	15·940
Magnesium carbonate, traces of alumina, phosphates, &c.	2·121
Insoluble in hydrochloric acid	34·344
	100·010

In further papers (*Comptes Rendus*, 1876, lxxxiii., pp. 76, 1184) M. Tissandier gives additional information upon some specimens of atmospheric dust, and especially upon those which fell on the Canary Islands, February 7th, 1863, at Syracuse, and in Italy on May 10th, 1872, and at Boulogne sur Mer, October 9th, 1876. Drawings are given to show the differences between such meteoric dust and the sands of the English Channel, and of the desert of Sahara. In the same volume, p. 364, there is also a note, by Mr. Phipson, of London, upon the presence of metallic iron in atmospheric dust.

(To be continued).

THE RARE EARTH CRUSADE: WHAT IT PORTENDS, SCIENTIFICALLY AND TECHNICALLY.*

By CHAS. BASKERVILLE, University of North Carolina.

In the movement of economic and social forces the closed century knew four periods of intensified activity. In 1775, a memorable date in American history, Watt began the manufacture of the steam engine. During the adolescence of our own country, revolutions were wrought in the commercial world by the invention of the locomotive by Trevethick (1801), the loom by Jacquard (1801), and Fulton steamed upon the Seine. By the beginning of the nineteenth century, the inventions of Watt and Boulton, Arkwright and Hargreaves, were completed, and something like the modern factory system was begun. From industrial history we gather that "England increased her wealth tenfold, and gained a hundred years' start in front of the nations of Europe."

While vigorous protests, some even violent, as the riots at Lyons and the destruction of Hargreaves' home in England, were made against this rampant spirit of industrialism, there was witnessed a literary renaissance in Great Britain, second only to "the spacious times of great Elizabeth." That age nourished Keats, Shelley, Byron, Scott, Coleridge, Wordsworth, Burns, and Burke. C. Alphonso Smith, in his exquisite essay on "Literature and Industrialism," says: "In a love of nature that made all seasons seem as spring, in devotion to democratic ideals, in variety of range and intensity of feeling, this period takes precedence of Elizabeth's reign." It was of this age that Wordsworth said :

> "Joy it was in that dawn to be alive,
> But to be young was very heaven."

Granting Tolstoi's definition of science as a "mere gratification of human curiosity," we realise that "science is history making," for it was in this period that Volta and Galvani (1801) gave us a source of power and a means of applying it. At the close of the time, Dalton had announced the atomic theory, and Davy had obtained the alkali and alkaline earth metals.

In the second period, about 1840, there accumulated the potentialities that shaped what is termed the Victorian Era. Quoting Smith again, "In those years, railroads first began to intersect the land, telegraph lines were first stretched, and the ocean was crossed for the first time by steam-propelled vessels. All these mechanical triumphs tended to annihilate time and space. The products of manufacture could now be sent with dispatch to the most distant quarters. Nations came closer together. The two hemispheres became, and have continued, one vast arena of industrial and scientific interchange. . . . ."

The literary record of this period contains the names of Tennyson, Goethe, and the Brownings as poets ; Dickens, Thackeray, and George Eliot in fiction ; Ruskin and Carlyle in miscellaneous literature. In America, during this Mexican war period, we had Longfellow, Lowell, Whittier, Hawthorne, Emerson, and Holmes, "the six names that have given the New England states their incontestable supremacy in American literature."

The part played by the south in literature during these periods was not prominent. The pre-eminence of that part of our country in forensic art and oratory need not be considered, nor need we discuss the social conditions and honest difference of opinion as to the proper interpretation of the true relationship of the government as a whole, and the integral states which constituted it, other than to say that the south, conquered, as was necessary, came out of the Civil War with new economic ideas, with a renewed and "ever-increasing development of her natural resources, with a more flexible industrial system, a more rational attitude towards labour, and more enlightened methods of education, and with it there came a literary and scientific inspiration impossible before." In the year 1870, our third period, which statisticians take as the birth year of the new industrial movement in the south, flashed out new literary stars, such as Sidney Lanier, Charles Egbert Craddock, and George W. Cable. That year can not be named in the presence of scientific men without our thoughts reverting at once to the names of Mendeleeff and Meyer.

The last period is but as yesterday, even to-day.

> "All the world's a stage
> And all the men and women merely players."

It has been called the age of trusts and mistrusts. In it we must realise that science and its applications must face vested interests ; these must be overwhelmed or its universal monopolistic rights be pigeon-holed by purchase. Let us realise, however, in this time, as Boyle has said, that "men often suffer as much cold and wet, and dive as deep to fetch up sponges as to fetch up pearls."

In 1788, Geyer discovered the new mineral, gadolinite, and in 1794, the Finnish chemist, Gadolin, separated a new earth, or oxide, in a black mineral found at Ytterby, near Stockholm, and called it yttria. In 1803, another Scandinavian mineral, then known as "the heavy stone of Bastnäs," or cerite, was discovered by Berzelius and Hisinger and Klaproth in Germany.

* A Lecture delivered before the Chemists' Club, New York, by request, April 8. From *Science*, of May 15, 1903.

In 1839, Mosander discovered lanthanum in this earth. Three years later he resolved it into two elements, one giving a white oxide and the other a pink, namely true lanthanum and didymium. Scheerer noted that yttria, which is white when heated in a closed vessel, becomes yellow when heated exposed to the air. He, in consequence, assumed that it was a complex substance, and the year following (1843), Mosander proved that it could be resolved into three earths, one being colourless (true yttria), the second rose-coloured (terbia), and the third (erbia) giving coloured salts, but a deep yellow peroxide.

H. Rose, in 1839, analysed samarskite and showed it to be a columbo-tantalate of iron and calcium on the one hand, and yttrium and cerium mainly on the other. Satisfactory analyses of this mineral, however, were not had for almost a half-century (Swallow, Allen, and Smith), when its comparatively abundant occurrence was noted in North Carolina.

Shortly after the discovery of the spectroscope, Gladstone, in 1859, observed the surprising fact that certain substances gave absoption spectra, especially didymium. This constituted the first important, and is now, perhaps, the most valuable criterion in the investigations of many of the rare earths.

In 1860, Berlin, by means of partial decomposition of the fused nitrates, showed the presence of but two earths where Mosander had reported three, namely, yttria, as given above, and a rose-coloured body, which was termed erbia. A reversal of names occurred, for two years later Bahr observed the characteristic absorption spectrum of erbia, and Delafontaine found it in Gadolin's yttria and Mosander's yellow peroxide. The typical oxide was assumed to be RO, and it remained for Mendeleeff in the enunciation of the Periodic Law (1870) to give lanthanum the present accepted formula for its oxide, La_2O_3.

These elements were obtained as metals—in the then accepted pure form—and Hillebrand and Norton determined the specific heats, which data have aided subsequent workers materially. These determinations, in the light of knowledge gained within recent years, possess a quondam value, however much care and energy may have been expended in securing them.

In 1878, Delafontaine stated that samarskite contained much terbia. He separated a more soluble formate and announced the new element philippium, which Roscoe, although he noted band λ 450, proved to be a mixture of yttrium and terbium. This band in reality belongs to dysprosium, discovered by Lecoq de Boisbaudran. The same year Delafontaine, having found a mare's nest in samarskite, from which Mosander separated erbium, announced decipium. The absorption bands attributed to this element were λ 416 and λ 478, which were subsequently appropriated by samarium, reported as a constituent of didymium by de Boisbaudran. Samarium would now have the name of decipium but for the fact, in 1881, Delafontaine declared his decipia could be resolved into an oxide, without absorption spectrum (true decipia) and one with these lines, or samarium.

J. Lawrence Smith, of Kentucky, in the seventies, announced mosandrum in samarskite. Marignac and Delafontaine independently pointed out that mosandrum was the same as terbium, while later de Boisbaudran demonstrated it was a mixture of terbia and gadolinia. This "nebula of elementary matter," as Petterson puts it in that charming account of the life work of Nilson, appeared to clear up through the work of the English, French, and Swiss chemists, Roscoe, de Boisbaudran, and Marignac. While "the beginning of creation is light," as Carlyle says, the millennium has not yet arrived, for the earths obtained from gadolinite began to break up into a number of new earths.

Cleve (1873) found that the bands of erbium with an atomic weight of 170·5 could be split into those belonging to one element, forming a red oxide with the characteristic emission spectrum (by incandescence) of old erbium and another group of two absorption bands in the visible spectrum. These were shown to belong to thulium.

Five years later Marignac found all the absorption bands could be eliminated by successive fractioning, whilst the atomic weight of the remaining oxide increased. This oxide gave colourless salts without absorption bands, and the name ytterbium was assigned to it, with an atomic weight of 172·5. In the erbia fractions Soret found bands which could not be attributed to erbium. This body, designated X, subsequently proved to be Clève's holmium.

Material giving out, Marignac, with the true scientific spirit, begged other and younger men to take up the work, using larger amounts. This Neilson did, and verified Marignac's work. Just before reaching the same point Marignac arrived at, however, Nilson obtained a nitrate of a less basic material of lower atomic weight. One fraction continued to drop, while the other rose until, in the year following (1879), assisted by Thalén, who examined the products with the spectroscope, Nilson separated probably the two best defined of the rare earths, scandium (44·1) and ytterbium (173). Nilson showed the location of these elements in the Mendeleeff table, the properties of the former having been predicted.

Referring to these elements Mendeleeff says :—"These metals, which are rare in nature, resemble each other in many respects, always accompanying each other, are with difficulty isolated from each other, and *stand together in the periodic system of the elements*." The last statement is based largely upon analogy, a most valuable method of argument in scientific generalisations without doubt, but, as Davy once said :—"Analogy is the fruitful parent of error."

In 1880 Marignac attacked samarskite, and by fractioning the double potassium sulphate obtained two oxides in almost pure state, as follows :—

Yα giving a white oxide, colourless salts, and no absorption bands. Six years later it was called gadolinium, and the atomic weight 156 assigned it by Marignac, de Boisbandran, Clève, and Bettendorff.

Yβ proved to be samarium of de Boisbaudran, or Delafontaine's original decipium. Marignac, Clève, Brauner, and Bettendorff determined its atomic weight (149—150). While the elementary character of samarium was questioned by de Boisbaudran and Demarçay as late as 1893, the latter stated that no real proof of the complexity of samarium had been offered. What an exquisite illustration we have here of Tyndall's dictum :—"Every system must be plastic to the extent that the growth of knowledge demands"; for, but a few years have passed before Demarçay (1901) announces europium, with atomic weight of 151 (approximately), obtained by prolonged fractionation of the double magnesium-samarium nitrate. His observations are reported as proved by reversal, absorption, spark, and electric phosphorescent spectra. The element appears to lie between samarium and gadolinium, with several strong lines in the violet and ultra-violet.

(To be continued).

A New Relation between the Electromotive Forces of Saline Solutions.—M. Berthelot.—The electromotive forces developed by the reaction of an acid on a base, and of the corresponding salt on the acid and the base which form it, are connected by a law which the author establishes by a number of experiments performed on six acids and two bases. He further discovers that the law thus established is only a particular case of a more general relation applicable to systems composed of three distinct electrolytes, such as A, B, AB. If E is the electromotive force in a cell containing solutions A and B separated by a porous pot, e_1 the E.M.F. in a cell containing A and AB, and e_2 the E.M.F. in a cell containing B and AB, then the relation $E = e_1 + e_2$ is generally true.—*Comptes Rendus*, cxxxvi., No. 23

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, June 17th, 1903.

Prof. W. A. Tilden, D.Sc., F.R.S., President, in the Chair.

(Concluded from p. 9).

102. "*The Acetoacetic Ester Synthesis.*" By A. C. O. Hann and A. Lapworth.

Within the last four years convincing evidence has been accumulated to show that Claisen's hypothesis (*Annalen*, 1897, ccxcvii., 92) as to the mechanism of the synthesis of β-ketonic esters and similar compounds by the use of sodium or sodium ethoxide is incorrect, and, moreover, the facts which led to the formulation of this theory have been shown by Dieckmann (*Ber.*, 1900, xxxiii., 2677) to be capable of a far simpler explanation.

The authors' observations, which are being extended, confirm the view that the acetoacetic ester synthesis is essentially the result of an addition process in which a metallo-organic compound becomes attached to the carbonyl group of an ester—

$$MeC(=O)OEt + \left\{ -CH_2\cdot C(=O)OEt \longleftrightarrow CH_2{:}C(O-)OEt \right\} Na =$$

$$= MeC(ONa)(CH_2\cdot CO_2Et)OEt$$

(compare Michael, *Ber.*, 1900, xxxiii., 3736; and Lapworth, *Trans.*, 1901, lxxix., 1269).

Ethyl bromoacetate was allowed to react with certain esters in presence of zinc and magnesium; with ethyl oxalate, good yields of ethyl oxaloacetate were obtained; with ethyl acetate, the product was mainly ethyl γ-bromoacetoacetate, the latter compound being produced by an exactly similar process, excepting that the reaction occurs between two molecules of ethyl α-bromoacetate without the intervention of ethyl acetate. Fittig, Daimler, and Keller (*Annalen*, 1899, ccxlix., 184) employed this modification of the acetoacetic ester synthesis in preparing diethyl ketipate (diethyl oxalodiacetate), but the complete analogy between the two methods appears to have hitherto escaped notice.

103. "*Rimu Resin.*" By T. H. Easterfield and B. C. Aston.

Rimu (*Dacridium cupressinum*; natural order, *Coniferæ*) is one of the most valuable of the New Zealand timber trees, the cracks or shakes in the heart-wood being nearly always partially or completely filled by a hard pink resin with a distinctly crystalline fracture.

The chief constituent (75 per cent) of the resin, a crystalline acid, for which the name *rimuic acid* is proposed, melts at 192—193°, distils with very slight decomposition at 296—300° under 21 m.m. pressure, and is optically active. It is easily soluble in alcohol or ether, and dissolves sparingly in water or light petroleum. Its formula, $C_{16}H_{20}O_3$, is supported by analysis, molecular weight determinations, titration values, and analysis of barium, lead, and silver salts. The barium compound is the most characteristic of the salts; it crystallises in well-defined, square plates having the composition $Ba(C_{16}H_{19}O_3)_2,14H_2O$. The alkali salts are very soluble and do not separate from solution in the presence of excess of alkali. Rimuic acid is lævorotatory, having $[\alpha]_D -159°$ in a 10 per cent alcoholic solution; it yields benzoyl and acetyl derivatives, and its formula may be thus represented: $C_{15}H_{18}(OH)\cdot CO_2H$. Like most of the acids from the pine resins, it yields no esters when treated with alcohol and hydrochloric acid.

The acid yields two crystalline nitro-derivatives when nitrated in cold glacial acetic acid solution.

104. "*Note on the Karaka Fruit.*" By T. H. Easterfield and B. C. Aston.

The kernel of the fruit of the Karaka tree (*Corynocarpus lævigata*; natural order, *Anacardiaceæ*), is a staple article of food amongst the Maoris and Morioris. In its raw state it is bitter and very poisonous, but when baked and subsequently soaked in water its toxic properties disappear. Examination of the kernels shows that they contain 15 per cent of a harmless, non-drying oil, and that the aqueous extract of the nut contains mannite, mannose, and dextrose. When the extract is distilled, it yields a considerable quantity of prussic acid. From the aqueous extract, Skey obtained a bitter glucoside, karakin, which, he stated, melted at 100, and obtained no nitrogen; the authors find, however, that karakin is highly nitrogenous, and when pure melts at 122°. It is most readily obtained from an alcoholic extract of the kernel by removing the alcohol under diminished pressure and re-crystallising the residue from warm water.

Karakin, which has the formula $C_{15}H_{24}O_{15}N_2$, crystallises in leaflets, and like amygdalin is only slightly toxic when removed from the enzymes with which it is associated. A second glucoside, *Corynocarpin*, can be obtained in small quantity by evaporating the aqueous extract at a temperature below 50° and extracting with ether. As this glucoside cannot be detected in the freshly prepared extract, and as the karakin disappears during the evaporation, it is probable that the second glucoside is a product of the partial hydrolysis of karakin. Corynocarpin crystallises in fine needles, melts at 140°, and is less soluble in hot alcohol than karakin.

105. "*The Slow Oxidation of Methane at Low Temperatures.*" II. By W. A. Bone and R. V. Wheeler.

The authors describe an apparatus for the closer investigation of slow combustion processes. This is essentially a closed system in which the reacting gaseous mixture can be circulated day and night continuously, at a uniform rate, (1) over a heated surface the temperature of which is kept constant, and (2) through suitable washing and cooling vessels for the removal of soluble or condensable intermediate products. A specially devised manometer allows of pressure records being taken at regular intervals, so that the velocity of the oxidation may be measured.

Further experiments with this apparatus on the interaction of methane (2 volumes) and oxygen (1 volume) at 450° and 500°, whilst they entirely confirm the authors' previous conclusion that neither hydrogen nor carbon is liberated at any stage of the oxidation, and that the final products consist simply of carbon monoxide, carbon dioxide, and steam, have proved the transient formation of formaldehyde as an intermediate product. In one experiment, 13 per cent, and in another as much as 22 per cent, of the methane burnt was obtained as formaldehyde which had been rapidly removed from the sphere of action by passing the reacting mixture through cold water each time it left the tube containing the heated surface.

The authors conclude that the oxidation of methane involves the following stages:—

1. The simultaneous formation of formaldehyde and steam, by the bimolecular reaction, $CH_4 + O_2 = CH_2O + H_2O$.

2. The further oxidation of this formaldehyde to carbon monoxide, carbon dioxide, and steam. This is probably effected as the result of the simultaneous occurrence of the following reactions:—

a. The bimolecular reaction, $CH_2O + O_2 = CO_2 + H_2O$.

b. The trimolecular reaction, $2CH_2O + O_2 = 2CO + H_2O$.

106. "*The Alkylation of Sugars.*" By T. Purdie and J. C. Irvine.

The method of alkylating hydroxyl groups by means of dry silver oxide and alkyl iodides does not appear directly applicable to aldoses or ketoses, and leads to oxidation and subsequent changes of some complexity; but α-methylglucoside and cane-sugar can be methylated by means of this reaction. α-Methylglucoside, when methylated in methyl-alcoholic solution, yields a mixture of methyl glucose ethers; the main constituent, trimethyl α-methylglucoside, which can be isolated by fractional distillation, is a viscid syrup; it boils at 167—170° under 17 m.m.

pressure, exhibits dextrorotation, and has no action on Fehling's solution.

Complete methylation of trimethyl α-methylglucoside is readily effected with silver oxide in methyl iodide solution, and under these conditions, tetramethyl α-methylglucoside is obtained as a comparatively mobile liquid boiling at 144—145° under 17 m.m. pressure; it is dextrorotatory, and has no action on Fehling's solution. Tetramethyl glucose, which is produced by hydrolysing the tetramethylated glucoside with dilute hydrochloric acid, distils without decomposition at 182—185° under 20 m.m. pressure, and solidifies slowly, and crystallises from light petroleum in tufts of radiating needles, melting at 81—83°; it behaves like an aldose, reducing warm Fehling's solution, giving tetramethylgluconic acid on oxidation, and reacting with phenylhydrazine in molecular proportion to form an oil, which is apparently a hydrazone. Tetramethyl glucose is dextrorotatory, but does not exhibit any notable multirotation.

The production from α-methylglucoside of a tetramethylgluconic acid, capable of forming a lactone, proves conclusively that the oxygen of the ring in the formula of the alkylglucosides is coupled with the γ-, and not with the β-carbon atom.

A pentomethylated glucose, isomeric with the tetramethyl α-methylglucoside already mentioned, is produced when a solution of tetramethyl glucose in methyl iodide is treated with silver oxide; it boils at 124—127° under 8 m.m. pressure, crystallises in slender prisms melting at 42—43°, and is lævorotatory.

Methylfructoside behaves like the corresponding glucoside, and, when completely methylated, yields tetramethyl methylfructoside; the two hydroxyl groups of acetone rhamnoside may also be methylated in a similar manner.

Cane-sugar, on methylation, yields a neutral oil, which has no action on Fehling's solution until it is hydrolysed. The products of hydrolysis are the above-mentioned crystalline tetramethyl glucose and an uncrystallisable syrup, which is probably the corresponding methylated lævulose.

The fact that methylated cane-sugar and methylated methylglucoside give on hydrolysis the same tetramethyl glucose proves that the constitution and linking of the glucose group of the disaccharide is the same as that of the simple glucoside, and affords conclusive evidence, at least so far as the glucose half of the molecule is concerned, of the correctness of Fischer's formula for cane-sugar (*Ber.*, 1893, xxvi., 2404).

107. "*Trimethyl α-Methylglucoside and Trimethyl Glucose.*" By T. Purdie and R. C. Bridgett.

When α-methylglucoside, in methyl-alcoholic solution, is methylated by means of dry silver oxide and methyl iodide, the chief product is trimethyl α-methylglucoside. In preparing this compound, it was found that, in addition to the low methylated derivatives, the tetramethylated glucoside was also produced, but only in small quantity, even when a large excess of the alkylating agent was used. The last hydroxyl group to be methylated undergoes the change more slowly that the others, and it seems therefore probable that the unmethylated hydroxyl of the trimethyl α-methylglucoside is that of the terminal primary carbinol group of the glucoside. The difficulty encountered in completing the methylation is, however, largely due to the loss of alkylating material caused by the production of dimethyl ether. Special experiments showed that the action between silver oxide and methyl iodide is much more rapid in the presence of methyl alcohol, and that the production of dimethyl ether is probably due, not to the direct interaction of the oxide and iodide, but to the methylation of alcohol.

The specific rotation of the trimethyl α-methylglucoside prepared by the authors was much in excess of that exhibited by the specimen referred to in the preceding note. The preparation of tetramethyl α-methylglucoside was also repeated and the substance was found to be more dextrorotatory than the specimens previously examined. The discordant results may be due to intramolecular rearrangement occurring under the action of methyl iodide, resulting in the production of varying quantities of the corresponding stereoisomeric β-glucosides.

By hydrolysing trimethyl α-methylglucoside with dilute hydrochloric acid, trimethyl glucose was obtained as a viscid, colourless syrup, which distilled without appreciable decomposition at about 194° under 9 m.m. pressure. The substance, which which was dextrorotatory and had the properties of an aldose, reduced Fehling's solution in the cold, and ammoniacal silver nitrate on slightly warming; it appeared to react with phenylhydrazine, but the product, which was an oil, could not be made to crystallise. On oxidation with bromine water, it yielded an oil boiling at about 160° under 11 m.m. pressure. The numbers obtained by analysis, and from the estimation of methoxyl, agreed approximately with those required for trimethylgluconic lactone. The lactonic nature of the compound was confirmed by its behaviour on neutralisation, and by the gradual change of optical activity exhibited by its solution.

108. "*Note on the Corrosion of an Egyptian Image.*" By Henry Bassett, jun.

An examination has been made of a bronze Egyptian image, about 6 inches high, and having a hollow base filled with lead. This figure probably dates from 200 to 100 B.C., and now bears a mutilated inscription which, according to Prof. Flinders Petrie, reads as follows:—"Khonsu give life to ——————, son of ————p, born of Saaenhap." It was found in the delta of the Nile, and is very extensively corroded, being covered by a thick, green coating, which in parts entirely replaces the original metal.

The material for analysis was obtained from the base of the figure, and the following analytical results were obtained:—

	Per cent.
Cu	50·65
Pb	6·74
Sn	2·94
Fe	0·15
Ni, Mn, &c.	0·11
Cl	15·71
SiO_2 (as sand)	1·14
H_2O	11·07
(NH_4)	0·11
	88·62

$CuCl_2$	29·34
CuO	46·10
H_2O	11·07
SnO_2	3·73
PbO	7·26
Fe_2O_3	0·22
NiO, &c.	0·14
SiO_2	1·14
NH_4Cl	0·32
	99·32

In the second table, the chlorine has been calculated as copper chloride, whilst the remaining copper and other metals are expressed as oxides.

Traces of calcium were also found, but the amount of sodium present was so small that it could only be detected by the flame test. If all the copper were present in the form of a basic chloride, $CuCl_2,3CuO,3H_2O$, corresponding with atacamite, this would require 26·84 per cent $CuCl_2$, 47·57 per cent CuO, and 10·78 per cent H_2O. It will therefore be seen that the substance produced by corrosion is less basic than atacamite. The formation of this mineral during the corrosion of copper and bronze articles when buried in the soil has been shown by Berthelot to be very general (*Comptes Rendus*, 1894, cxviii., 768), but although the formation of this basic copper chloride is in most cases due to the action of the sodium chloride in the soil

(Berthelot, *loc. cit.*), yet in the present instance, ammonium chloride may have played the most important part, since the latter salt was found in amount sufficient for estimation, whereas the former was not.

109. "*Contributions to the Chemistry of the Terpenes.* Part I. *The Oxidation of Pinene with Chromyl Chloride.*" By G. G. HENDERSON, T. GRAY, and E. SMITH.

When dissolved in carbon disulphide, chromyl chloride and pinene combine to form a solid compound, $C_{10}H_{16}.2CrO_2Cl_2$, which is decomposed by water, and yields a brown, oily liquid. This liquid, when distilled in steam, yields a quantity of resin and a volatile oil (Etard, *Comptes Rendus*, 1893, cxvi., 434). The authors have found that the oil contains a saturated *aldehyde*, C_9H_{15}·CHO, an unsaturated *ketone*, C_8H_{14}:CO, and a small quantity of a chlorinated oxidation product of pinene. The aldehyde, which is a crystalline solid with a characteristic odour, melts at 32—33° and boils at 205—207° (under 755 m.m. pressure); it is insoluble in water, but readily miscible with alcohol and ether. The *semicarbazone* crystallises in pearly leaflets, and melts at 191°. The aldehyde rapidly undergoes spontaneous oxidation in the air, being converted into a saturated *acid*, C_9H_{15}·CO_2H. This acid, which is obtained by oxidising the aldehyde with either boiling dllute nitric acid or aqueous potassium permanganate, crystallises in leaflets or flat prisms, and melts at 117°; it is only sparingly soluble in cold water, but very readily so in alcohol, and volatilises slowly in steam. The *lead* salt and the *silver* salt are obtained as white precipitates; both are soluble in boiling water, but the latter very sparingly.

The ketone is an almost colourless, aromatic liquid, which boils at 206—207° under 774 m.m. pressure; its refractive index is 1·4760. The ketone at once decolorises permanganate, and combines additively with 1 mol. of bromine; it yields an oily *oxime* and a crystalline *semicarbazone*, which melts and decomposes at 226—228°; on oxidation with sodium hypobromite, it gives bromoform and *p*-toluic acid.

*110. "*Some Physical and Chemical Properties of Strong Nitric Acid.*" By V. H. VELEY and J. J. MANLEY.

The investigations published by W. N. Hartley in the current number of the *Transactions* (p. 658) on the absorption spectra of nitric acid in various states of concentration, have induced the authors to place on record certain physical and chemical properties of nitric acid varying in concentration from 78 to 100 per cent HNO_3 in continuation of their former work (*Proc. Roy. Soc.*, 1901, lxix., 86, and *Phil. Mag.*, 1902, [6], iii., 118).

Although such properties as density, contraction, refractive indices, and electrical conductivity vary uniformly with percentage concentration from 78 to 92 per cent, yet from this point to 100 per cent there is an exceptional alteration in the variation, reaching a maximum at about 96 per cent, this strength corresponding with an acid which, according to Hartley's view, might be indicated by the formula $3H_2N_2O_6,H_3NO_4$ (=95·9 per cent HNO_3).

Acid having this concentration appears to form a kind of eutectic solution, and therefore presents an analogous, although not strictly parallel case to that of sulphuric acid containing 98 per cent H_2SO_4, which has been shown by R. Knietzsch (*Ber.*, 1901, xxxiv., 4069) to be a point of critical concentration as regards density, contraction (compare Pickering, *Trans.*, 1890, lvii., 74), electrical conductivity, chemical reactivity, vapour pressure, and, to a less degree, capillarity and viscosity.

As regards chemical properties, certain qualitative experiments have been made on the direct nitration of cotton by nitric acid of approximately 100 per cent concentration without the addition of sulphuric acid.

111. "*Notes on Ozone.*" By J. K. H. INGLIS.

Experiments have been made in order to ascertain the molecular state of ozone when dissolved in acids. In the first place, it was found that the amount of ozone present in an acid solution could be determined by means of the following reaction: — $O_3 + 2HBr = Br_2 + O_2 + H_2O$, the bromine liberated being estimated by potassium iodide and sodium thiosulphate.

In the second place, an investigation of the solubility of ozone in water showed that the solution could not be brought into equilibrium with respect to the gas, since some of the latter was always decomposed on being bubbled through the solution, although the concentration of the latter remained constant. Hence the molecular state cannot be ascertained by means of the solubility relationship.

Lastly, some experiments made on the action of ozone on hydrogen peroxide indicated that these substances acted slowly on one another, manganous sulphate behaving as a catalyser.

Erratum.—Vol. lxxxvii., p. 269, col. 2, line 16 from bottom, for "ammonia," read "methylamine."

PHYSICAL SOCIETY.

Ordinary Meeting, June 26th, 1903.

Dr. R. T. GLAZEBROOK, F.R.S., President, in the Chair.

THE meeting was held, by invitation of Dr. Waller, in the Physiological Laboratory, University of London.

Dr. WALLER gave a demonstration of the Effect of Light on Green Leaves.

The origin of these researches was the result of the consideration of the retinal effects after light stimulation, and the wish to have a sensitive surface naturally spread out for examination. The effect of light is to produce a current (of an E.M.F. of the order of 0·01 volt), at first from the illuminated to the dark parts in the leaf, and later (or as an after-effect) from dark to illuminated. These currents are apparently an index of two opposite processes in the leaf, *i.e.*, dissimilation and assimilation, and give very close analogies to the analogous processes in animal tissues (*e.g.*, Nerves).

Dr. WALLER also demonstrated the "Blaze" currents in Animal and Vegetable Tissues.

These are seen when a strong exciting current (such as an induction-shock of sufficient voltage) is led through a pair of non-polarisable electrodes, and these are then connected with a galvanometer. An electrical response (of greater energy than the exciting current) is given in a direction commonly homodrome to the latter, *i.e.*, in the reverse direction to the ordinary polarisation counter-currents. This "blaze" response is the algebraic sum of post-anodic and post-kathodic currents; the resultant is commonly homodrome, but an anti-drome blaze, distinguished from polarisation by its much greater order of magnitude, is also seen.

Dr. WALLER also showed two methods for the Quantitative Estimation of Chloroform Vapour in Air.

The first was by receiving the mixed gases into a flask of known capacity, absorbing the chloroform by means of olive oil, and reading the reduction of pressure by a manometer. The second was by the simple weighing of a light flask, first filled with air, then filled with mixed air and chloroform vapour. As each litre of the latter is 4·032 grms. heavier than the same bulk of air, by choosing a flask of 250 c.c. each observed milligrm. of increment is equal to 0·1 per cent of chloroform vapour. Any sized flask can be used, and corrections made for temperature and pressure by the formula :—

$$\log P \text{ per cent} = \log m \text{ (milligrms.)} + \log P \text{ (m.m. Hg)} - \log T° (\textit{absolute } T°) - \log v \text{ (volume in c.c.)} + 1·8392 \text{ (a constant)}.$$

Dr. N. H. ALCOCK exhibited a method of determining the Temperature-limits of Nerve Activity in Warm-blooded and Cold-blooded Animals.

The higher limit was obtained by immersing the isolated nerve in 1·05 per cent NaCl solution. It lies between 40°

C. and 42° C. in the frog, 48° and 49° in the mammal, and is at 53° in the bird, corresponding closely to the coagulating-point of the tissue proteids. The lower limits were obtained by cooling the nerve-chamber as a whole, and taking the temperature of the nerve with a compensated thermo-junction. The limits were $-3{\cdot}5°$ C. for the frog, $+3{\cdot}8°$ C. for the mammal, $+6{\cdot}8°$ C. for the bird, giving a range of nerve-action of 45° C. to 46° C. for all animals. The method, therefore, permits of an hitherto impossible analysis of actually living nerve-substance.

Prof. AYRTON expressed his interest in the communications, and said he hoped it would be possible to arrange a meeting of the Society at which the points arising from the papers might be discussed.

Two papers by Dr. HARDY, (1) "*On the Movement of Unionised Bodies in Solution in an Electric Field*," and (2) "*On the Passage of Nervous Impulse through the Central Nervous System*," were postponed.

NOTICES OF BOOKS.

A Text-book of Organic Chemistry. By WILLIAM A. NOYES. New York: Henry Holt and Co. 1903. Pp. 534.

THE most radical departure from the method of treating this subject as adopted in other text-books is, the author tells us, the dropping of the division into "fatty" and "aromatic" compounds; this arrangement may be justified by the fact that so many connecting links are now known between the two classes of bodies that they no longer stand isolated from each other, but we are afraid that the introduction of the new classification will bring about some confusion in the minds of young students when they hear other chemists speaking of the "fatty" and "aromatic" series of compounds.

The subject of organic chemistry is so vast and is growing so rapidly that few can hope to keep pace with it. This adds to the difficulty of teaching: there is such an accumulation of matter that it becomes difficult to know what to omit and what to insist upon. However, the student will do well to *read* everything carefully, and to thoroughly master certain portions that will be pointed out to him by his instructor.

The present volume is divided into twenty-five chapters, the earlier ones being on such general subjects as purification, analysis, molecular weights and formulæ, physical properties, &c.; then come the hydrocarbons, all classes of them together, as mentioned above. The oxygen compounds come next, followed by those compounds containing halogens, nitrogen, and sulphur; finally there are three chapters upon heterocyclic compounds, alkaloids, and compounds of physiological and pathological interest.

The index appears to be very full, covering over fourteen pages of two columns each.

CORRESPONDENCE.

RUSTING OF IRON.

To the Editor of the Chemical News.

SIR,—An evident error occurs in a letter of mine which you were good enough to print in the CHEMICAL NEWS (vol. lxxxvii., p. 311).

The formula quoted should be $Fe_2O_2(OH)_2$. By a slip of the pen this appears as $FeO_2(OH)_2$. I should be sorry to seem to attribute so remarkable a composition for rust to Prof. Dunstan.—I am, &c.,

BERTRAM BLOUNT.

76—78, York Street, Westminster,
June 27, 1903.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 23, June 8, 1903.

Formation of Alcohol in Fermenting Saccharine Liquids.—Armand Gautier and G. Halphen.—During the process of alcoholic fermentation the ammoniacal nitrogen almost entirely disappears; the basic organic nitrogen increases or remains tolerably constant, whilst the albumenoid ammonia undergoes no sensible variation; the total nitrogen diminishes and the volatile acidity increases all through the process. This acidity, which is always less than 0·1 grm. per litre in grape juice, when it becomes greater than 0·15 grm. per litre, taken in conjunction with the fact of the almost complete disappearance of the ammoniacal nitrogen, constitutes the best method of identifying the fermenting liquor. In grape juice a small proportion of cyclic and non-cyclic organic bases are found which increase in proportion as the fermentation proceeds. Traces of glycerin exist in grape juice, and during regular fermentation these increase in proportion to the alcohol formed.

Action of Arsenic on Copper.—Albert Granger.—Copper combines easily with arsenic when heated in a current of arsenic vapour mixed with an inert gas. A white mass is obtained, which is very brittle and of metallic appearance, and fuses at a red heat. At a temperature of 440° the arsenide of copper, Cu_5As_2 is formed; at a lower temperature, the lower arsenide, Cu_3As.

Qualitative and Quantitative Analysis of Iridium Osmides. — MM. Leidié and Quennessen. — Already inserted.

Hypothesis as to the Nature of Radio-active Bodies. — Filippo Re. — The author believes that the particles constituting the atoms of radio-active bodies have been previously free and that they constitute a nebulous formation of extreme tenuity. These particles in time become re-united round their centres of condensation, giving rise to infinitely small suns, which, by a method of ulterior contraction, take stable and definite forms which make up the atoms of the elements which we know, and which we may compare to small extinct suns. The larger suns which are not yet extinct constitute the atoms of radio-active bodies. The author puts forward various facts in support of this theory.

Curves of Dissociation.—A. Bouzat.—The author's experiments on dissociation curves lead him to the conclusion that, if all the invariant systems in which a solid body dissociates into another solid body and a gaseous body are arranged in the same group, the variation in the entropy which results from the liberation of a molecule of gas under a definite pressure is the same for all the systems of the group.

MISCELLANEOUS.

Physical Society.—A Special General Meeting of the Fellows of the Physical Society will be held at the Royal College of Science, South Kensington, on July 13th, 1903, at 5 p.m., when the subjoined Resolution, which was passed at the Special General Meeting of Fellows held on June 26th, will be submitted for confirmation as a Special Resolution:—"That the Articles of Association contained in the printed document submitted to the Meeting, and, for the purpose of identification, subscribed by the Chairman thereof, be, and the same are hereby approved: and that such Articles of Association be, and they are hereby, adopted as the Articles of Association of the Society."

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th

inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the chair. The following were elected members:—Lord Oxmantown, Mr. R. S. B. Hammond Chambers, K.C., Mr. M. B. Field, Mr. H. D. McLaren, Mr. G. Marconi, Mr. R. Pearce, Mr. E. P. S. Roupell, and Mr. W. Wavell. The special thanks of the members were returned to the Misses Gladstone for their present of a portrait of Dr. John Hall Gladstone, F.R.S.

The Allotropism of Tellurium.—D. Biéliankine.—The author has observed that tellurium precipitated from an alkaline solution, and considered by Berthelot to be amorphous, has a density greater than that of the tellurium precipitated from an acid solution by sulphurous acid; these two modifications have not the same appearance. The tellurium precipitated by sulphurous acid is a very finely-divided, black, amorphous powder; the tellurium precipitated by the addition of water and the cooling of a concentrated boiling alkaline solution, is a dark-looking powder containing a number of silvery-looking flakes formed of microscopic rhombohedra. It may be admitted, therefore, that of the three modifications observed by Berthelot, one is amorphous and the other two crystalline. The author found their densities to be as follows:—1. *Amorphous Tellurium Precipitated from an Acid Solution by Sulphurous Acid.*—d varied from 5·973 to 6·081; after heating to 430°, d varied from 6·036 to 6·201. 2. *Tellurium Fused and Cooled Slowly.*—d varied from 6·298 to 6·381; after having been heated to 430°, d varied from 6·291 to 6·336. 3. *Tellurium Precipitated from an Alkaline Solution.*—d =6·072 to 6·213; after heating to 430°, d=6·061 to 6·158. 4. *Tellurium Fused and Cooled Rapidly.*—d=6·099 to 6·223.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiii., p. 670.

Influence of the presence of Cerium in Lanthanum containing Didymium and Praseodymium. — R. Marc.—While engaged in the fractionation of didymium by the action of chlorine on the hydrate suspended in an alkaline medium, the author has been led to the following conclusions:—Oxide of didymium is grey in colour when it is perfectly free from cerium, otherwise it is brown. Below 2 per cent, cerium can only be detected in didymium by the colour of the oxide, and no longer by means of peroxide of hydrogen or persulphate of ammonium. The amount of peroxide contained in a brown didymium poor in praseodymium, is proportional to the amount of cerium it contains, provided the latter is not very much. If the proportion of cerium exceeds a certain limit the oxidation extends, not only to the praseodymium, but also to the neodymium; but in the absence of praseodymium, the neodymium is no longer oxidised by cerium. Lanthanum and neodymium prevent the oxidation of praseodymium. In the absence of these two metals the praseodymium is immediately and completely peroxidised by the least trace of cerium; but the smallest quantity of lanthanum or praseodymium retards the oxidation considerably.—*Berichte*, vol. xxxv., p. 2371.

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2277.

NOTE ON THE EFFECT OF EXTREME COLD ON THE EMANATIONS OF RADIUM.*

By Sir WILLIAM CROOKES, F.R.S.
and
Professor JAMES DEWAR, F.R.S.

As it seemed advisable to examine the action of extreme cold on the action of radium, the following experiments have been made in continuation of work formerly done by either of us separately.

The first endeavour was to ascertain whether the scintillations produced by radium on a sensitive blende screen were affected by cold.

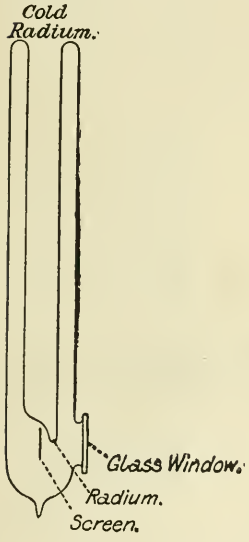

Fig. 1.

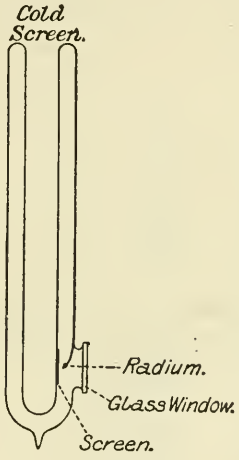

Fig. 2.

A small screen of blende with a morsel of radium salt close in front was sealed in a glass tube, and a lens was adjusted in front so that the scintillations could be seen. On dipping the whole into liquid air they grew fainter and soon stopped altogether. Some doubt was felt whether this might not have been caused (1) by the presence of liquid, (2) by the screen losing sensitiveness, or (3) by the radium ceasing to emit the heavy positive ions. To test this two tubes were made, in one of which the radium salt could be cooled without the screen, and in the other the screen could be cooled while the radium salt was at the ordinary temperature. The accompanying sketch explains their construction.

1. Radium salt cooled by liquid air, Fig. 1. Screen at ordinary temperature. Scintillations quite as vigorous as with radium at the ordinary temperature, the screen and radium being *in vacuo*.

2. Radium at the ordinary temperature and screen cooled in liquid air, Fig. 2. As the screen cooled the scintillations became fainter and at last could not be seen. On allowing the temperature to rise the scintillations recommenced.

3. A screen with a speck of radium salt in front of it was sealed in a tube. Water was put in the other end of the tube and the tube sealed on the pump, A good exhaustion was kept up and the water boiled away, the vapour being condensed in phosphoric anhydride. The tube was sealed off when a few fine drops of water were still remaining in the tube. The scintillations were well seen in this saturated aqueous vapour. The lower end of the tube was dipped in liquid air, which instantly condensed the aqueous vapour and left a very good vacuum. On now examining the scintillations they were if anything brighter and more vigorous than at first. When liquid hydrogen cooling was used instead of liquid air the action was equally marked, showing that the highest vacuum that can be obtained by the action of cold does not diminish the scintillations.

In the upper part of the tube, away from the radium and screen, two platinum wires were sealed to show the state of the vacuum. The spark passed easily at the ordinary temperature, showing a reddish line of aqueous vapour. When the other end of the tube was in liquid air the spark refused to pass.

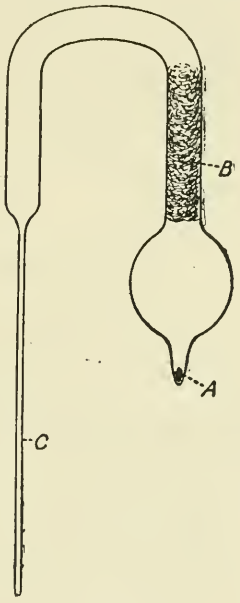

Fig. 3.

4. It was thought that perhaps the passage of the induction spark might have liberated some occluded hydrogen, so another tube similar to the above was made without the platinum wires. Here also immersion in liquid air, if it had any effect, brightened the scintillations, and on replacing the liquid and cooling by liquid hydrogen no change was observable.

In order to test the activity of radium in rendering air electrically conductive, some radium bromide was sealed up in a glass tube and heated to the highest temperature the glass would stand, during the production of as high a vacuum as the mercurial pump would give. The whole tube was then immersed in liquid hydrogen contained in a vacuum vessel. On bringing the radium in such a vessel into a room in which a charged electroscope was placed, it began to leak when the tube of radium surrounded with liquid hydrogen was some 3 feet away, and was very rapid in its action when a foot away from the electrometer. On immersing the tube containing the liquid hydrogen with submerged radium in another large vessel of liquid air and bringing the combination near the electroscope, the action was the same.

The luminosity of the radium salt in liquid hydrogen was much more marked with the pure compound than had been formerly observed with the diluted mixtures containing large quantities of barium salts.

* A Paper read before the Royal Society, May 28, 1903.

Professor Rutherford and Mr. Soddy have made the important discovery that a condensable emanation is diffused into gases from solutions of radium salts, which is capable of condensation from the gas mixture at the temperature of liquid air. As it was important to ascertain what was taking place in this respect with the anhydrous radium bromide when isolated in the highest vacuum, the following experiment was arranged :—

A glass apparatus of the shape represented in Fig. 3 was constructed. The part marked c is a fine capillary drawn out tube some 5 or 6 inches in length, the B portion, about 2 inches long, being filled with hard-pressed purified asbestos. The radium salt was located at A, and the whole was most carefully heated, exhausted to the limit of the mercurial pump, and sealed off. In the dark no trace of phosphorescence could be seen in any part of the apparatus unless from the pieces of the radium bromide. The fine tube c was now immersed in liquid air in a large flask, so that distillation might proceed undisturbed for days. After twenty-four hours of this operation, on looking at the part c while covered with the liquid air, a marked phosphorescence was recognisable owing to some condensed emanation. The luminosity became naturally more marked the longer the time the action was allowed to proceed, and it is our intention to continue the experiments for a lengthened period of time, and then seal off the fine capillary part so that the condensed product may be thoroughly examined.

THE SPECTRA OF NEON, KRYPTON, AND XENON.*

By E. C. C. BALY,
Lecturer on Spectroscopy in University College, London.

The gases were illuminated by the passage of the discharge from an induction coil through them under reduced pressures. Vacuum tubes were filled with each one of them, and the glowing gas in a capillary portion was examined "end on" through a quartz window. Considerable difficulty was experienced in the use of the vacuum tubes, owing to the rapid absorption of the gas by the electrodes when the electric current was kept passing for long periods. It was found that when the gases were quite pure, and free from any diatomic impurities, the aluminium electrodes were readily volatilised, an aluminium mirror being formed upon the immediately surrounding walls of the tube ; at the same time the electrodes became very hot, and it was necessary to make them of very stout wire, *e.g.*, No. 12 B.W.G. Special care had to be taken in making each individual electrode so as to enable it to withstand the disintegrating action of the discharge. The unusual heating of the electrodes gave rise to considerable trouble on account of the large quantities of hydrogen evolved from them ; it is a common experience to anyone, when filling a new vacuum tube, to find a quantity of hydrogen given out by the electrodes; this hydrogen, as is well known, may be readily removed by further exhaustion. If, however, into a tube from which this hydrogen has been removed, a small quantity of one of the monatomic gases be introduced, a further large quantity of hydrogen is evolved from the electrodes. Every trace of this second quantity of hydrogen must be removed before the tube can be depended upon ; it is necessary to thoroughly wash out the tube by repeated admission of argon and re-exhaustion.

The measurements were all made upon photographs taken with a Rowland concave grating of 10-foot radius and 14,438 lines to the inch ; the first three orders of spectra were employed, and nearly all the chief lines were measured in two orders. As far as can be estimated by the coincidences between the different spectra, the probable error is less than $\pm 0{\cdot}003$ Angström unit. The spectra are all composed of bright lines and are absolutely characteristic in each case. While neon possesses only one spectrum, krypton and xenon both have two, one being given when the ordinary discharge is passed and the other when a Leyden jar and spark gap are placed in the circuit ; this second spectrum is much more complex than the first in each case, an analogy being thus shown with argon.

There are about forty lines of weak intensity common to the jar and spark gap spectra of krypton and xenon ; this may possibly be considered as evidence of the existence of another element of higher atomic weight in the same series.

In the tables of the spectra, columns are given of the measurements which have appeared by Liveing and Dewar and by Runge in the case of krypton. A very satisfactory agreement is to be observed between the two series of measurements, although those of Liveing and Dewar are only given to the fourth place. It is interesting that these authors give, in their list of the spectrum lines of the most volatile gases of the atmosphere, about 162 lines which do not appear on the neon photographs, and, therefore, in all probability, do not belong to this gas.

The most important lines in the visible region of the spectrum are given in the following tables :—

Wave-lengths.	Intensity.	Wave-lengths.	Intensity.
Neon Spectrum.			
6402·40	10	6096·37	10
6383·15	8	6074·52	10
6328·38	6	6030·20	10
6304·99	8	5975·78	8
6266·66	10	5974·73	6
6217·50	8	5944·91	10
6182·37	10	5882·04	8
6163·79	10	5852·65	20
6143·28	10	5764·54	8
6128·63	8	4259·53	6
The First Krypton Spectrum.			
5871·12	10	4454·12	10
5570·50*	10	4400·11	6
5562·45	6	4376·33	10
4671·40	10	4362·83	9
4624·48	10	4319·76	10
4502·56	9	4318·74	8
4501·13	7	4274·15	10
4463·88	10		
The Second Krypton Spectrum.			
5633·17	6	4109·38	6
4765·90	6	4098·89	7
4762·60	5	4088·48	8
4739·16	7	4067·53	5
4659·04	5	4065·22	8
4634·05	5	4057·17	8
4619·31	6	4050·62	5
4615·46	5	4044·80	5
4577·40	6	3998·10	5
4523·32	5	3994·98	6
4475·18	7	3954·90	5
4355·67	10	3920·29	8
4317·98	5	3917·76	6
4300·67	5	3912·69	5
4293·10	6	3906·37	8
4145·28	6		
The First Xenon Spectrum.			
4923·28	6	4524·83	6
4916·63	6	4501·13	10
4807·19	6	4193·70	8
4734·30	8	4116·25	7
4697·17	7	4109·84	5
4671·42	10	4078·94	10
4624·46	15	3967·74	10
4582·89	5	3951·16	10

* Probably the green Aurora line.

* Abstract of a Paper read before the Royal Society, June 18, 1903.

The Second Xenon Spectrum.

Wave-lengths.	Intensity.	Wave-lengths.	Intensity.
6097·80	7	4603·21	10
6051·36	7	4592·22	6
6036·40	6	4585·65	10
5976·67	7	4577·36	6
5751·28	5	4545·34	8
5727·15	5	4541·03	8
5719·83	6	4532·67	5
5667·85	6	4524·38	5
5659·67	5	4481·01	7
5616·99	6	4462·38	20
5531·33	7	4448·28	10
5472·90	7	4434·35	6
5460·63	6	4415·00	7
5450·71	5	4406·99	5
5439·19	8	4395·91	10
5419·40	10	4393·34	10
5372·62	8	4330·63	15
5339·56	9	4296·52	5
5314·15	8	4245·54	10
5292·40	10	4238·37	10
5262·16	5	4223·14	5
5260·65	5	4215·77	5
5191·60	5	4214·17	5
5080·88	7	4213·80	5
4921·68	6	4208·61	6
4890·24	5	4193·25	8
4887·47	5	4180·20	10
4883·68	6	4158·14	5
4876·68	7	4145·85	5
4862·69	8	4109·20	6
4844·50	10	4057·55	5
4823·47	6	4050·19	6
4698·20	5	3992·98	5
4683·76	5	3950·70	8
4652·15	6	3922·67	10
4615·72	5	3908·00	7

The total numbers of lines measured in the five spectra are as follows :—

Neon	164 lines
Krypton I.	74 „
Krypton II.	700 „
Xenon I.	92 „
Xenon II.	1370 „

There, 17 lines which are common to the two Krypton Spectra, and 7 common to those of Xenon.

THE RARE EARTH CRUSADE: WHAT IT PORTENDS, SCIENTIFICALLY AND TECHNICALLY.*

By CHAS. BASKERVILLE, University of North Carolina.

(Concluded from p. 19).

In 1883 Crookes brought into consideration phosphorescent spectra obtained in a vacuum tube under the influence of an electric discharge. The year following, Lecoq de Boisbaudran obtained another method of securing a phosphorescent spectrum. It is, in fact, an inverse spectrum, nearly related to that of Crookes, very delicate, being greatly influenced by small amounts of foreign bodies and other conditions. The brilliancy of the bands thus obtained does not depend upon the proportion of the active substance present. A small amount of the body with much inert material gives a bright spectrum, consequently it offered little promise as a method for following the process of fractionation.

Up to this time holmia and thulia had not been freed from the other earths. In 1886, de Boisbaudran showed that holmia was composed of true holmium (162) and dysprosium (?), adverted to, characterised by several bands, the one to which Sir William Crookes called especial attention being λ 451·5. This Englishman later (1889) subjected yttrium salts to a great number of fractionations, several thousand, finding the bands of the original material distributed among the different fractions. From this work he assumed that yttrium could be split into a number of elementary substances, which he termed "meta-elements," naming one victorium after the lamented Queen. Without doubt Sir William Crookes enunciated in this paper an important principle in inorganic research, namely, what may be termed "partial cleavage"; that is, the fractioning of a complex mixture of elements may be pushed to an extreme with one compound, and the bodies appear elementary. On applying another method, or the same method to another compound, of the assumed elementary substance, the cleavage may be brought about in another direction, and so on. The "genesis of the elements" was the natural theory offered by that master-mind. It was strongly combated in the main, however, by de Boisbaudran, who showed that two of the bands obtained, $Z\alpha$ and $Z\beta$, are not at all related to yttria, as the former follows holmium and the latter is identical with terbium. He says, further :—"Perfectly pure yttria gives no phosphorescent spectrum." Dennis, the American worker on the element in question, appears to agree with the French chemist.

It may be recalled that Delafontaine extracted samarium (his original decipium) from Mosander's didymium. The theoretical work referred to naturally gave rise to the complexity of didymium, which has an absorption spectrum characterised by a number of well-defined bands. In fact, Clève made the prediction of the presence of another element in lanthanum and didymium in 1878. Carl Auer (von Welsbach), in 1885, by prolonged fractional crystallisation of the double ammonium nitrate, obtained from the pink solution green salts of praseodidymium (140), and rose-red salts of neodidymium (143). The absorption spectra of these two are complementary. The next year, Crookes eliminated band after band of the didymium until only λ 443 remained. Krüss and Nilson, and Kieserwetter and Krüss, prepared didymium from several sources, fractioned the preparations, and arrived at a similar conclusion. It is now known, as shown above, that erbium has been resolved into seven other well-characterised elements, viz., besides erbium (166·3), scandium (44·1), yttrium (89), terbium (160), ytterbium (173), thulium (170·7), holmium (162), and dysprosium (?). After the elimination of samarium, didymium shows at least nine distinct absorption bands :—λ 728·3, 679·4, 579·2 to 575·4 (which is easily resolved into two), 521·5, 512·2, 482, 469, 445·1, and 444·7 (443) (ultra-violet and infra-red not considered). In short, these two elements, neo- and praseodidymium, consist of at least nine elements. The full conclusion of Krüss and Nilson may be stated in their own words :—"Nach obigen Auseinandersetzungen hätten wir an Stelle des Erbiums, Holmiums, Thuliums, Didyms, und Samariums die Existenz von mehr als zwanzig Elementen anzunehman."

While the acceptance of such conclusions without question would be wholly unscientific, we must carefully consider the general idea involved, and the investigations upon which the conclusions were founded, and the investigations carried out subsequently to test them, Absorption bands determined under variable conditions are not to be accepted as essential characteristics of new elementary substances, as they have been shown to vary with the salts used. Sorby and Liveing have shown that the character of the solvents and traces of impurities bear importantly upon the intensity of the absorption bands. Lawrence Smith and de Boisbaudran, and latterly Dennis and Chamot, have called attention to variations in the absorption spectrum of didymium, when nitric acid is present. Becquerel showed there were variations in the spectra o

* A Lecture delivered before the Chemists' Club, New York, by request, April 8. From *Science*, of May 15, 1903.

crystalline compounds of the same element. Very recently Muthmann and Stützel have shown that if a substance be regarded undecomposable, its absorption spectrum varies considerably with dilution and amount of free acid present. Demarçay has urged the necessity of giving the thickness of the medium used, with a statement of its strength.

C. M. Thompson reported that didymium salts from various sources showed no material differences in absorption spectra. Schottländer remarks, however, that the material used contained several oxides, giving absorption bands, so the intensity of certain bands of a particular element may have been increased by the superposition of bands of other elements.

Crookes and Dennis independently made the extremely interesting observation that the heavy orange bands (575—579), which were resolved by Auer, were not altered in their fractions when the remaining lines had undergone some changes, hence the former stated that probably "didymium will be found to split up in more than one direction, according to the method adopted." The work of Dennis on the relative intensities of the bands observed, by varying the procedure of fractionation, is in direct accord with the observations of previous investigators as to the compound nature of neo- and praseodidymium.

Von Scheele (1898) carried out a series of investigations looking toward the proof of the elementary character of praseodidymium. Bettendorff, by a spectroscopic examination of the mother-liquors obtained by the Welsbach method, confirmed the observations of Krüss and Nilson, especially with regard to the absorption bands in the blue portion of the spectrum. Schottländer working with the same object in view, came by no means to the same conclusion. He held it probable that praseodidymium consists of a mixture of two elements, whose oxides burned in air give R_2O_3 and RO_2 (*i.e.*, $R_2O_3 + 2RO_2 = R_4O_7$, the accepted peroxide). His conclusion was founded upon the small per cent of oxygen present in the peroxide. Forshing confirmed Bettendorff's results spectroscopically, and reported Pr α characterised by the yellow bands, and Pr β, which has the three bands in the blue, indigo, and violet. Boudouard arrived at the same conclusions. Brauner concluded, in his work on the oxides, "from the tendency of them both (praseodidymium and neodidymium) to become more highly oxidised than would correspond to the formulæ Pr_2O_4 and Nd_2O_5, that praseodidymium and neodidymium may be further split up."

Von Scheele maintains that none of the savants has proved Krüss and Nilson's theory that there are four elements present in praseodidymium. By long repetition of the Welsbach process he failed to bring about any variation in the yellow bands, which Bettendorff maintained could be fractioned away, and demonstrated to his own satisfaction the elementary composition of praseodidymium in a paper reciting much careful and patient experimentation. Unfortunately, he ignored the work of Crookes and Dennis, which is dependent upon variation of the finer details of manipulation. In our laboratory, following entirely novel lines of research for this element, we have apparently verified the conclusion of the complexity of the element in question.

The material used was generously presented by Mr. H. S. Miner, the long-time associate and successor of the lamented Shapleigh. It was quite free from neodidymium, but contained a notable amount of lanthanum. The presence of lanthanum facilitates the fractioning of didymium by the Auer method, as pointed out by Dennis. A pure praseodidymium compound is readily had by using the method of Baskerville and Turrentine, namely, fractioning a citric acid solution saturated with the hydroxide, and heating. The citrate obtained was converted into the oxide. This oxide was free from the other elements giving absorption bands in the visible spectrum. So far we have not been able to examine the ultra-violet, but shortly expect the arrival of one of Wood's nitrosodimethylaniline screens, which I am having made for my spectroscope. The instrument is a Steinheil plane grating (made by Brashear) with 14,438 lines to the inch, essentially the same as that described by Dennis in his work with Dales on yttrium, except a size larger. It was purchased by a grant from the Bache Fund of the National Academy. The oxide was proved to be free from elements which give no absorption band, especially lanthanum, by means of photographs of the arc spectrum obtained with a Rowland concave grating (15,000 lines to the inch and twenty-one-foot diameter). The spectrograph work was done by my friend Dr. W. J. Humphreys, of the Department of Physics, University of Virginia, and will be published by us in full at the proper time. The oxide was very carefully treated with hydrochloric acid, bringing about partial solution, whereby a distinct brown oxide was obtained different from the normal black peroxide; further, a separation has been secured by fusion with sodium peroxide.

Other methods of attack have been followed, as, for example, fractional crystallisation from a concentrated chloride solution by means of gaseous hydrogen chloride, fusing with alkaline hydroxides, sodium dioxide, &c. The details will be given in the full papers when published.* Suffice it to say that we have succeeded in obtaining a preparation which has lost entirely the absorption line λ 443, and another, very small in amount, which shows only that line. The oxide is bright green when heated in the air. The work of Crookes and Dennis is thus verified by entirely novel methods. Drossbach reports the existence of an element in monazite sand with an atomic weight of 100; that is, eka-manganese, but it is discredited by Urbain.

It may be interesting at this point to call the attention of the scientific men of America to the fact that from the locality, Ytterby, where cerite was found, four elements, yttrium, erbium, terbium, and ytterbium, have secured a name. From the occurrence of samarskite and monazite (Mitchell and McDowell, and other counties in North Carolina and Brazil), which contain most of these rare earths, and have furnished so much of the material for the researches, not a single element is named, except the tentative carolinium, which will now receive attention.

The other rare earths to which I wish to direct your indulgent attention in a few words are those which possess radio-activity, a property accidentally re-discovered by Becquerel. It may be remarked that Sir George Stokes fifty years ago addressed the physicists of the British Association on the curious action of certain bodies in emitting light at ordinary temperatures. Little was then known of the phenomenon of fluorescence. There is not time to attempt a discussion of the origin and nature of radio-activity. It appears that our satisfactory Maxwellian theory of the progression of ethereal stresses may yet be harmonised with the older corpuscular view of Descartes and Newton by the recent elegant researches of Becquerel, J. J. Thomson, Rutherford, Giesel, and others.

M. and Mdme. Curie have been pioneers in utilising this physical activity, which serves to detect the presence of minute amounts of certain elements contaminating hitherto well-defined bodies. J. J. Thomson, in his recent extremely interesting address at Belfast, brings out a point demanding the chemist's closest attention, namely, that the radio-activity is five thousand times as delicate as the spectroscope, it matters not whether the arc, spark, absorption, or phosphorescent spectrum be made use of.

By prolonged fractionation the Curies separated radium from barium salts. Demarçay has prepared the spectrograph showing the characteristic lines of the element, while Mdme. Curie determined its atomic weight (225). It fits beautifully in Mendeleeff's table. The Curies have also announced polonium, or the active constituent of bismuth. Uranium appears to have been the first to show this property, as noted by Becquerel. Actinium, it seems, is the

* I have been assisted in the numerous researches, barely summarised in this address, by Messrs. J. E. Mills, R. O. E. Davis, J. W. Turrentine, James Thorpe, Reston Stevenson, W. O. Heard, Hazel Holland, E. B. Moss, H. H. Bennett, Geo. F. Catlell, and F. H. Lemly. The separate papers will shortly be published. Three grants of fifty dollars each have been made by the American Association for the Advancement of Science to aid in the work on the rare earths.

elusive body found in pitchblende by Curie, and appears to be the same as Crookes's uranium X.

Chroustschoff a dozen years ago announced that thorium contained another element, which he called russium. I have been unable to secure a copy of this paper or even to learn where it appeared. I am informed by Prof. Mendeleeff, who mentions it in his "Principles of Chemistry," that Chroustschoff made the announcement before the Russian Chemical Society, but had published no complete investigation. Two years ago, Brauner, working along one line, and I, on another, independently announced the complexity of that element.

It is generally accepted now from the published work that the property of emitting rays which affect the photographic plate is not a specific property of thorium, but characteristic of a constant contaminating constituent of that element. It is well known also that, while some of these radiations or emanations affect the photographic plate, some do not. The electrical method of measurement (quantitative) has been substituted in our work, and improved methods of fractionation are being used, whereby we seem to be approaching a non-radio-active thorium and one possessing that property in high degree. Further, similar compounds of thorium fractions similarly treated show almost no difference with the Rowland grating referred to, yet show marked divergence in their radio-active properties. The radio-active work is being done by Mr. G. B. Pegram, of the Department of Physics in Columbia University.

I have not come from "away down south" to the centre of commercial activity of all the Americas to tell you how these rare substances are to be had at low cost, advertise their uses, form a combination, and arrange for their sale at a good profit, although one of my neighbours ranks high among Knickerbocker mergers. The fourth period in rare earth activity is co-existent with the extension of the use of some of them for illuminating purposes. The price of thorium nitrate fifteen years ago was over five hundred dollars per pound. Now the market price is about five dollars per pound. Commerce required thorium compounds; they were provided. Commerce demanded thorium compounds at a reasonable price; the demands were met. The prices of certain of the impure rare earths occurring in nature with thorium are high, but their values do not follow well-known economic laws, and are purely fictitious. When uses are found, the prices of these by-products will fit the demand.

In this maze of an enticing problem one imagines much, and many speculate more. Not unfrequently, especially of late, have we been treated with irenic disquisitions as to the location of these rare elements in the natural system. It appears to be forgotten that Mendeleeff used his table to correct the formulæ of the typical oxides of certain elements, as, for example, lanthanum (LaO to La_2O_3). The fact is forgotten that the atomic weights now ascribed would be materially different were the type different. The ascribed atomic weights are dependent upon the synthesis or analysis of the sulphates almost without exception. It is forgotten that "-yl" salts, like uranyl, chromyl sulphates, are possible for these elements, as recently shown by Blandel for titanium and Matignon for praseodidymium and neodidymium. Furthermore, it is forgotten that the sulphate method is absolutely defective, as Schützenberger pointed out. This has been verified by Wyrouboff, Dennis, Brauner and Pavlicek, and Damarçay, as well as myself. Therefore, all attempts to arrange these elements, some of which are known to be complex, in the periodic table are veriest speculation, which can profit little. It is quite as true also that the table should receive no discredit because it fails to account for them with our present knowledge. According to its author the table reserves twenty-three places for their occupancy.

Two desiderata may be mentioned:—1. Satisfactory tests, preferably colorimetric, which may be quickly applied, as Hillebrand has remarked about titanium. This supplied, perhaps these earths would not be so rare. I have shown the universal occurrence of titanium. 2. Spectral data from more highly purified substances, for much that is now at hand has been obtained from impure earths.

The methods of attack at present are mainly based upon the same phenomena of oxidation, reduction, and saturation. The applications are different, however. As typical examples, a few may be cited as follows:—Melikow has been using the hypochlorites, virtually the Lawrence Smith method; Muthmann, hydrogen dioxide and acetate solutions; Dennis is using organic acids, as did Metzger for thorium; Jefferson and Allen have applied certain organic bases for analytical purposes, while in our laboratory we have saturated the stable alkalis, fused with sodium peroxide, and reduced with such basic reducing agents as hydrazine and phenylhydrazine, and so forth.

All is not dark, for rifts in the clouds are making. Old Watt said:—"Nature has always a weak side, if we can only find it out." Looking back and with that century of experiences we can frequently in a measure judge of the future, and those things which make toward the true end.

Naturally a sequel is due this paper, and I look forward to presenting it in my Vice-Presidential Address before Section C of the American Association at the St. Louis meeting. Some sequels are better than their predecessors; Most of them, however, are not so good.

ON THE RADIO-ACTIVE EMANATION IN THE ATMOSPHERIC AIR.*

By J. ELSTER and H. GEITEL.

I.

On the Origin of the Radio-active Emanation contained in the Air of the Ground.

By H. Geitel.

One of the objects to which we have directed our attention since the last conference at Göttingen has been the elucidation of the abnormal amount of radio-active emanation contained in the air of cellars and caves, with which its high ionisation is very closely connected. This might conceivably be due either to an as yet unknown power of stagnant air of giving rise to such emanation spontaneously, and of storing it up in itself, or to a diffusion of the latter from the surrounding walls and from the soil. Many facts may apparently be brought forward in favour of the first assumption of a self-activity, namely the actual spontaneous rise of the conductivity of hermetically sealed quantities of air, and the failure of all efforts to discover a trace of primary radio-activity in the material of the walls of cellars and caves.

Experiments with a greater quantity of air, which was shut up for some weeks in a boiler, showed, however, that no appreciable accumulation whatever of radio-active emanation occurred during this time.

So there only remained the assumption that the walls of the subterranean spaces, or the air diffusing from the surrounding earth through their pores, were the carriers of the emanation. It was, in fact, afterwards proved that the air removed by simple suction from the soil at our dwelling place was charged with active emanation, and that its activity actually exceeded that of the air of cellars and caves. (We have already published these results in *Physikal. Zeitschrift*, 1902, iii., p. 574). By the investigations of Ebert and Ewers, this property has been demonstrated in the case of the air from the ground of Munich also (H. Ebert and P. Ewers, *Physikal. Zeitschrift*, 1902, iv., p. 162).

How far the nature of the soil at the place of observation influences the activity of the air contained in it was then the next point to be examined.

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* Aus der Denkschrift der Kommission für luftelektrische Forschungen, München, 1903.

Here also two different assumptions might be made. Either that activity was a universal property of the air of the ground independent of the nature of the soil, or it was the result of a certain amount of primarily active substance contained in the material of the soil itself. While, in the first case, samples of air of any origin (so long as they undoubtedly consisted of the air of the ground) must show equal activity, in the second case, an inequality of the activity was to be expected, as it could hardly be supposed that the inducing active substance would be present in the soil with the same activity in all places.

Some results obtained previously pointed to the last alternative.

Thus the conductivity of the air in cellars and caves, measured by means of the leakage apparatus, showed in different places considerable differences, which could only be explained as being due to the influence of the containing walls. Thus we found high ionisation of the air in the cellars of our dwelling place (about six times the normal), and in the Baumanns and Iberg caves, in the Hartz (nine and three times the normal),* but a considerably smaller ionisation in cellars in Clausthal, in the Hartz, and in Zinnowitz, on the Baltic Sea (from 1·3 times to twice the normal). In a large space in a potassium chloride mine at Vienenburg, in the Hartz, the ionisation of the air was actually less than in the free atmosphere, but here the conditions were certainly unfavourable, as the air contained distinct traces of the fumes of the blasting materials.

In connection with this, an experiment at Clausthal, in the Hartz, was, however, specially instructive. An insulated copper wire, negatively charged by means of an influence machine, was held for an hour in free air, and another in a cellar; the activity excited was, in the case of the first, eleven times greater than in the case of the latter. Thus here the free air actually contained more active emanation than that of the cellar, a condition of things which is completely contradicted by previous experience.†

Hence it was most probable that samples of the air of the ground of different origin would have different activity. In order to obtain more definite grounds for this opinion, it was necessary to find a method of removing the air from the ground of different places, and of comparing the activity of these samples. As it is not generally practicable to perform the test for radio-activity on the spot, the samples must be securely sealed in easily transportable vessels. The time necessary for removal to the place of examination, as long as it only amounts to a few hours, is without appreciable effect on the result; an interval of two or three days was even allowed for longer distances, when it was only a question of confirming results by rough experiments. If a longer time elapses between filling the transport vessel with the sample of air and examining the latter, the activity is found to have become too small, and after about four weeks it had disappeared in a sample obtained from Wolfenbüttel. For the removal of the air from the ground, an egg-shaped vessel of three litres capacity was employed; it could be closed at both ends by means of well-fitting cocks. Before being used it was filled with water, and held vertically with both cocks shut. The upper opening was connected, by means of rubber tubing, with a measuring tube about 1 m. long; this was driven into the soil until only a few c.m. projected. When the cocks were cautiously opened, the water flowed out through the lower, while the air from the ground passed in through the upper. When the vessel was completely filled with the air, both cocks were hermetically closed.

To perform the investigation, we allowed the air to pass through water into a bell-glass of about 30 litres capacity; beneath the bell-glass was placed a leakage apparatus, without the protecting cover (*Cf.*, *Physikal. Zeitschrift*, *loc. cit.*), surrounded by wire gauze. The quantity of electricity escaping in a given time served as a standard for the ionisation of the air which was introduced into the bell-glass. Before every experiment the bell-jar was filled with the air of the room, and the loss of electricity was determined before the admission of the air of the ground, and also at the end of each series the loss in the case of the electroscope. This last was always so small that it could be neglected throughout, since the whole method employed was somewhat inaccurate.

With the potential of 100 to 200 volts employed, the saturation current beneath the bell could be regarded as reached. The fall of potential in 15′ in ordinary air, the mean value of which amounted to 14 volts, is henceforward adopted as unit for the ionisation of the air beneath the bell after the introduction of the sample to be examined. This ionisation can also be taken as a standard for the amount of radio-active emanation.

By the method thus described, we have examined samples of air from different places. Those which were obtained from the clayey and limestone soils of the gardens in Wolfenbüttel were strongly active, though not all equally (activity on the given scale lay between 16 and 4). A sample taken from a gravel pit in the neighbouring wood was decidedly less active (activity = 3). The air from the ground at Wolfenbüttel had the same activity as a sample from Göttingen (activity = 12). A sample from the clay slate of Blankenburg-a-H. was much less active (activity = 2·3); the activities of the air from the shell limestone of Würzburg,* and from the basalt of Wilhelmshöhe, near Kassel, were still smaller (activity = 1·6 and 1·01 respectively). These results were sufficient to show that the nature of the soil from which the air was drawn must have a considerable influence on its activity, and the next thing to do was to seek for a primary radio-activity of its constituents.

As has already been mentioned, our earlier attempts as well as those of Ebert and Ruf (*These Sitzungsprotokolle*, May, 1902; also *Physikal. Zeitschrift*, 1902, iv., p. 93), to prove the existence of a primary Becquerel radiation in the materials of the walls of cellars and caves, were certainly unsuccessful, but in these experiments, only the building materials and the solid rock were examined, and not the loose soil itself. We now filled a zinc dish, of diameter 29 c.m., and height 2·5 c.m., with earth which had been dug up from some centimetres below the surface of the garden of our house, and introduced it under the bell-glass described, in such a manner that the electroscope rested with the enveloping wire gauze on this earth.

Immediately an undoubted increase in the ionisation of the air beneath the bell became apparent, as must be expected in the presence of a feebly radio-active substance; in the course of from two to three days this rose to a maximum value of about three times the normal. It did not matter in this experiment whether the earth was in the moist condition in which it was removed, or whether it was introduced underneath the bell-glass after protracted drying; after the lapse of eight months no decrease of activity was apparent in the material used for the first experiments. The soil from the field and from gardens situated outside the town behaved in the same way as that from our garden, and a grayish blue clay from a pit in the neighbourhood was also active; but, on the other hand, a white quartz sand (containing limestone) was inactive.

The next thing to do was to make an attempt to separate off the inactive substances of the soil by chemical means, and thus concentrate the activity in smaller masses. The clay, which formed a homogeneous mass after washing away the coarser lumps in it, seemed to be most suitable for this purpose. By extraction with dilute hydrochloric acid all the calcium carbonate present could be completely removed, and the residue, after drying, immediately showed a lower activity than before the treatment; but this increased in a few days (during which the substance was

Dr. Cuomo, of Capri, kindly informed us that he has observed also abnormally high leakages (about three times the normal) in some stalactite caves there.

† We take this opportunity of heartily thanking Prof. Gerland, of Clausthal, who rendered this experiment possible.

* Our thanks are due to Dr. Harmo, of Würzburg, for sending us samples of air from that place, and from Göttingen.

kept outside the bell-glass) to about the original amount. Again digesting with hydrochloric acid, or dilute sulphuric acid, at first caused a decrease of the activity, but this also was restored in course of time. Unfortunately, on account of the great quantities of the substance to be treated, it was not possible for us to evaporate to dryness the liquid which had been in contact with the clay quickly enough to examine the residue for radio-activity, but from the behaviour here described, there seemed to us to be no room for doubt that an active substance was present in the clay which we examined ; this, like thorium oxide, according to Rutherford and Soddy's researches (E. Rutherford and F. Soddy, *Phil. Mag.*, 1902, p. 370), forms a more strongly active substance soluble in acids (comparable with Rutherford's ThX) which after extraction with acids is gradually regenerated. The same phenomenon as in the case of clay we found also in the so-called cave loam (Loess) from the Baumanns caves in the Hartz.

In order to have better defined substances to deal with, we also examined washed chalk, ground heavy spar, pure commercial potter's clay, sea salt, and Karlsbad salt for Becquerel radiation. The results were generally negative, traces being suspected in the case of the clay alone, but in any case it is inferior to the garden soil, as well as to the clay of Wolfenbüttel and the Loess. On account of the chemical similarity of radium and barium, we thought that we might expect to find some activity in heavy spar, as possibly traces of the first element might accompany the latter ; the idea that Karlsbad salt is obtained from great depths of the earth induced us to examine it, whilst the sea salt, as an example of a soluble substance, might perhaps also contain radio-active constituents.

Ashes of plants which had grown on active earth also gave no appreciable Becquerel radiation.

The result of these researches is thus the proof of a certain radio-activity of the soil itself; this remains attached to the clayey constituents of the soil on treatment with dilute acids. We have not succeeded in further separating or completely isolating the active principle.

We were much pleased to hear of a confirmation of this result by Cooke, recently communicated by Rutherford (E. Rutherford, *Nature*, 1903, lxvii., p. 511), according to whom a perceptible very penetrating radiation is said to be given off from brick.

Before attempting to concentrate the active substance distributed throughout the naturally occurring clay in only very small quantities, which is very difficult owing to the large amount of substance which must be employed, it was first to be considered whether this activity is chiefly primary, and not merely induced in the clay by contact with the air from the ground, in which case the origin of the activity in the latter would still remain unexplained. The behaviour of the clay towards acids, which agrees with that of the primarily active substances as well as the persistence of its activity, are certainly arguments against the last assumption, but still we did not think it unnecessary to examine generally whether neutral bodies, on being buried in the earth, *i.e.*, after lengthy contact with the air of the ground, could assume an appreciable induced activity.

We used for this purpose ground heavy spar, whitening, pure nearly inactive potters' clay, and cotton. Each of these substances was wrapped in linen, and surrounded with a covering of iron wire gauze, and placed some 50 c.m. below the surface of the ground and left there at least four weeks. The wire gauze served to hold together the covering of linen, which became disintegrated in the earth, so that an adulteration of the substance with the soil was prevented. After being dug up, the heavy spar, whitening, and cotton showed no appreciable activity, but the activity of the clay was unmistakable. By its diminution in course of time, which moreover was different in different samples, it was clearly shown to be induced activity.

It is a noteworthy coincidence, which also rendered the further examination more difficult, that the clay which contains the primarily radiating substance which acts inductively on the air of the ground, is itself excited to secondary radiation by this air.

We will now briefly report on some further experiments which partly supplement the above results and partly only confirm them.

If we brought some kilogrammes of earth into a closed space of about 40 litres capacity, and introduced a metal wire charged to – 2000 volts, after the lapse of some hours the induced activity might easily be proved by means of a leakage apparatus. If we sucked the air through a greater quantity of earth placed in a metal receptacle, and allowed it immediately after leaving the earth to enter the bell-glass which covered the leakage apparatus under the protecting wire gauze, it had always an abnormally high conductivity, which, however, disappeared after a few minutes, as soon as the current of air ceased. Hence, we must assume that the current of air in passing through the earth was ionised by its Becquerel radiation, in the same way as when it flows over an active Röntgen tube. The fact that we had to deal not with a simple ionisation of this kind, but rather with a taking-up of active emanation from the earth, was shown when we led the air before its entrance into the bell-glass through a metal tube, of diameter 1·5 c.m. and length 10 c.m., in the axis of which an insulated wire was stretched ; the tube and the wire were connected with the poles of a high tension pile of about 1600 volts. The air thus flowed in a powerful electric field, by which either some free ions must be completely removed, or at any rate their number must be much diminished. However, no alteration in the loss of electricity resulted under the bell-glass, whether the electric field was established or not. Hence the phenomenon must be explained by the assumption that the air in passing through the earth takes up a small quantity of active emanation, which rapidly becomes inactive. If the air is allowed to pass through inactive material, such as heavy spar or chalk, neither action appears.

Following a suggestion of Herr Bodländer, of Brunswick, we also investigated the natural carbonic acid gas which is evolved from great depths of old volcanic soil, with regard to the active emation it contains. We had sent to us a steel flask full of such natural carbon dioxide in the liquid state, from the carbon dioxide works of Schoor and Wolter, at Burgbrohl on the Rhine, immediately after it had been filled.

Although five days elapsed before the flask reached us, the gas when brought underneath the above-mentioned bell-glass was decidedly ionised. It followed on the one hand from the duration of the conductivity of the gas (which persisted for some days), not taking into account the defects of unipolar conduction, and on the other hand, from the possibility of secondarily rendering active a metal wire negatively charged and introduced into it, that we were not dealing with an excitation of electricity caused by the contents of the flask frothing out, or by the friction of the little drops on the opening, but with a genuine radio-activity. After the expiration of sixteen days the gas taken from the flask, which was still almost full, was inactive, and now behaved like artificial carbon dioxide which was generated from sodium bicarbonate and dilute sulphuric acid, and which was introduced beneath the bell-glass through a cotton-wool filter, in the same way as the natural gas.

The carbon dioxide arising from the earth thus carries with it an active emanation, exactly like the air contained in the capillaries of the earth. It would be interesting to investigate for the same property the gases arising from deep wells and thermal springs, immediately after their appearance at the surface of the earth.

In order to have always at our disposal a larger volume of the air charged with the earth emanation, we had a bell of strong sheet iron, of about 1¼ cub.m. capacity, and tubulated at the top, buried with its lower edge 25 c.m. beneath the surface of the earth in the garden of our house. By diffusion, the equality of the activity of the air shut up

under the bell with that of the soil soon showed itself when the tube was closed.

The strong activity which we observed by means of wires which were insulated and negatively charged and sunk through the tube, led us to treat phosphorescing bodies in the same way, as we expected to observe in these distinct light phenomena.

When we introduced into the bell on a dark night a carboard cylinder covered with Sidot's blende, which had been previously kept for days in the dark and showed no phosphorescence, and charged it negatively to 2000—3000 volts for some hours, on being taken out of the bell it showed a decidedly feeble phosphorescence, which, however, was plainly visible in a perfectly dark room.

On closer examination of the phenomenon, we observed that characteristic scintillating luminosity which has already been described by us, and by Sir Wm. Crookes (W. Crookes, *Nature*, 1903, lxvii., p. 522; J. Elster and H. Geitel, *Physikal. Zeitschrift*, 1903, iv., p. 439), and which is caused by the unceasing appearance and disappearance of countless points of light on the blende.

The thought at once occurred to us that these scintillating points represented the places at which negative electrons are hurled off from the radio-active layer covering the zinc blende. Sir Wm. Crookes, who observed the same thing when he brought a radium preparation near a screen covered with Sidot's blende, on the other hand regards them as the places at which the electrons hurled off by the radium hit the surface of the screen. Even if both conceptions are still purely hypothetical, we must regard ours as being more probably correct, because in our experiment, with the exception of the phosphorescing surface, no radio-active body was generally present, and thus a movement of electrons towards the latter did not generally occur.

(To be continued).

TWENTY-FIRST ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee on Indexing Chemical Literature, appointed by your body at the Montreal meeting in 1882, respectfully presents to the Chemical Section its Twenty-first Annual Report, covering the twelve months ending June 1, 1903.

Works Published.

"An Index to the Literature of Thorium (1817—1902)." By Cavalier H. Joüet, Ph.D. Smithsonian Miscellaneous Collections, No. —. Washington, City, 1903.

"References to Capillarity to the End of the Year 1900." By John Uri Lloyd (aided by) Sigmund Waldbott. Bulletin No. 4 of the Lloyd Library of Botany, Pharmacy, and Materia Medica, Cincinnati, Ohio, 1902. 212 pp. 8vo.

The 665 "references" extend from 1519 to 1900; each is accompanied by a summary of the contents of the paper cited.

The Journal of the American Chemical Society. "General Index to the First Twenty Volumes, 1879—1898, and to the *Proceedings*, 1877—1879." Easton, Pa., 1902. 237 pp. 8vo.

Though issued anonymously the Preface bears the initials of E. W. Morley and O. F. Tower, and the labour was one of love. Accuracy of detail and adequate treatment on every page are its admirable features. Besides an index of Authors and an index of Subjects there is an index of Obituaries which is suggestive. Also an index of new books.

Notes on Foreign Bibliographies,

"A Bibliography of Steel-works' Analysis," by Harry Brearley, forms an Appendix to the volume entitled "The Analysis of Steel-works' Materials," by Harry Brearley and Fred. Ibbotson. London, 1902.

This Bibliography comprises 1858 references, which occupy more than 130 pages 8vo. The items are grouped under seven heads, besides minor sub-divisions; the literature is, however, very incomplete, being confined to four British journals.

"A Catalogue of the Library of the Chemical Society [of London]." Arranged according to Authors with a Subject Index. London, 1903. 8vo. 324 pp.

"International Catalogue of Scientific Literature." First Annual Issue [for the year 1901]. D. Chemistry. Published for the International Council by the Royal Society of London. London, 1902. Vol. II. Part I. June, 1902.

Works in Progress.

A Second Supplement to the "Select Bibliography of Chemistry," by Dr. H. Carrington Bolton, has been completed, and accepted by the Smithsonian Institution for publication. It brings the literature down to the end of the year 1902.

An "Index to the Literature of Cadmium" has been begun by Prof. Ernest N. Pattee, of Syracuse University.

An "Index to the Literature of Glucinum" has been begun by Prof. Chas. L. Parsons, of New Hampshire College, Durham, N.H.

An "Index to the Literature of Germanium, Gallium, and Indium," has been begun by Dr. Philip E. Browning, of New Haven, Conn.

Mr. Frank R. Fraprie, writing from Munich, Bavaria, reports substantial progress on an "Index to the Literature of Lithium, Cæsium, and Rubidium."

Mr. Benton Dales is engaged on an "Index to the Literature of the Yttrium Group of the Rare Earths." His address is Ithaca, N.Y.

Committee:—

H. Carrington Bolton (in Europe),
F. W. Clarke (in Europe),
Albert B. Prescott,
Alfred Tuckerman,
H. W. Wiley.

June 1, 1903.

* Advance sheets from *Proceedings of the American Association for the Advancement of Science.*

METEORIC DUSTS, NEW SOUTH WALES.*

By Prof. A. Liversidge, LL.D., F.R.S., University of Sydney.

(Continued from p. 18).

In an account of his expedition to Greenland in 1870, Prof. A. E. Nordenskjöld states (*Geological Magazine*, 1872, p. 355) that at the bottom of the holes in the ice he found a grey powder, to which he gave the name of cryoconite (κρύος, ice, and κόνις, dust); he found it on inland ice as well as on the shore ice; Nordenskjöld concluded that it was not derived from the disintegration of the rocks in the district, but from meteoric sources, especially as it contains particles of metallic iron bearing cobalt, copper, and probably nickel. Prof. Nordenskjöld describes it as occurring in layers some millimetres thick, and often conglomerated into small loose balls, and under the microscope as being principally made up of white angular transparent particles, intermixed with vegetable fragments as well as particles of what appear to be felspar and augite.

Dr. G. Lindström obtained the following analytical results from a sample :—

* Read before the Royal Society of N.S. Wales, September 3, 1902. From the *Journal and Proceedings of the Royal Society of N.S. Wales*, vol. xxxvi., p. 241.

Cryoconite.

Silica	62·25
Alumina	14·93
Iron sesquioxide	0·74
Iron protoxide	4·64
Manganese protoxide	0·07
Lime	5·09
Magnesia	3·00
Potash	2·02
Soda	4·01
Phosphoric acid	0·11
Chlorine	0·06
Water, hygroscopic, at 100° C.	0·34
Water and organic matter at a red heat	2·86
	100·12

When long digested with strong sulphuric acid 7·73 per cent dissolved and 16·46 per cent when treated with strong hydrochloric acid. The organic matter seems to have been mainly due to the presence of various minute algæ. Particles of metallic iron have on several occasions been found in snow collected in places where there was no possibility of the iron having been derived from surrounding habitations.

In December, 1871, Nordenskjöld collected some snow near Stockholm, after five or six days consecutive fall, which on melting left a black soot-like residue containing metallic particles; to remove any possibility of doubt, Dr. Karl Nordenskjöld collected snow from off the ice of the Rautajerwi, on March 13, 1872, at Evoia, in Finland, separated by a thick forest from any houses (Dr. Walter Flight, "History of Meteorites," *Geological Magazine*, 1875, p. 157). The residue left on melting was soot-like in appearance, and under the microscope was seen to contain black carbonaceous particles, with yellowish-white granules and black magnetic grains, but the quantity was insufficient to determine the presence of cobalt and nickel. But snow collected by the Arctic expedition on August 8th, 1872, on the drift ice in Lat. 80° N. and Long. 30° E., yielded particles of metallic iron; also on September 2, in Lat. 80° N. and Long. 15° E., freshly fallen snow collected from the ice-field yielded from 0·1 to 1·0 m.grm. of black magnetic particles to the cubic metre of snow; iron, cobalt, and phosphorus were detected, and probably nickel was present also; the portion insoluble in acid contained fragments of diatoms and minute transparent angular particles.

Dr. Moss speaks of similar dust ("Voyage to the Polar Sea, in H.M.S. *Alert* and *Discovery*," Capt. Sir G. Nares, vol. ii., p. 61):—"Occasionally deposits of atmospheric dust were to be met with throughout the stratified ice, sometimes scattered in very minute points, which, when examined, proved to be air cells coated with the impalpable dust, sometimes occurring in comparatively conspicuous quantities in lines cutting the stratification and marking what had once been the bottom of a superglacial lake. Similar dust was to be found on the present surface of the floes, occasionally greatly magnified in appearance by the growth amongst it of an alga (*Nostoc aureum*). The dust often occurred in little granules, so that in mass it formed an oolite. . . . All the specimens of ice dust obtained by me from the floe bergs are undoubtedly the air carried débris of crystalline rock not traceable to the neighbouring shore."

On February 26, 1883, a fine dust was discovered in the snow in Trondhjem Amt, in North Norway. Dr. Reusch, of the Mineralogical Faculty of the Christiania University, found that it was not of volcanic origin as had been imagined, but that it consisted of fine particles of quartz sand, horn-blende, and talc, mixed with very fine particles of vegetable matter. The dust must have been carried a very long distance, the whole of the country having been for months covered with deep snow. The wind blew strongly from N.N.W.

In 1873, Prof. Nordenskjold obtained rounded grains of metallic iron from hail which fell in Stockholm, other observers had done the same as far back as 1821; Cozari had, in 1834, shown the presence of nickel in the iron brought down by hail.

Dr. Henry Rink, writing from Christiania, Norway, (*Nature*, Dec. 13, 1883) draws attention to the fact that the ice of icebergs which are made up of ancient snows ought to yield large quantities of Nordenskjöld's cosmic dust, although he had never observed its presence in such ice.

Reichenbach found traces of cobalt and nickel in the soil from the Lahisberg, in Austria, from the Haindelberg, Kallenberg, and Dreymarksteinberg, and nickel in the soil of the Marchfeld Plain (Dr. Flight, *Geological Magazine*, 1875, p. 162); the hills consist of sandstone and limestone, and are free from mineral veins. Haidinger suggested that impoverished soils when allowed to lie fallow acquire a fresh supply of phosphorus from such meteoric dust.

In the report for 1882 of the Committee of the British Association appointed for the purpose of investigating the practicability of collecting and identifying meteoric dust, &c., drawn up by Prof. Schuster, it is stated that the dust falls frequently observed in the Atlantic, the southern parts of Italy, and sometimes in the Red Sea, were at one time supposed to be of meteoric origin, but it has now been conclusively proved that the dust has its origin in the sandy deserts of northern Africa, whence it is carried by the winds often through considerable distances, the grosser particles falling down first, so that ultimately only the finest remain in suspension. Although these dust storms are of terrestrial origin, yet they carry magnetic and other particles which are of meteoric origin (see Tissandier's "Les poussières de l'air," Paris, 1877).

Amongst the magnetic particles found in the dust are some which are perfectly spherical; these have been found in the snow of Mont Blanc, at a height of nearly 9000 ft., and in the dust collected at various other places. The spherical particles have evidently been fused—no similar ones have ever been found in volcanic dust; the smoke from factory chimneys does contain similar particles, but such contain neither nickel nor cobalt, whereas Tissandier found both these metals in the magnetic particles collected at the Observatory of Saint Marie-du-Mont. "We are therefore driven to assume a cosmic origin to these particles."

Prof. Schuster examined the sand from the desert near the Great Pyramids and found magnetic particles present in the proportion of 1 in 144,000. Most were angular and evidently derived from magnetic rocks; but with them were also some perfect spheres of iron, similar to those described by Tissandier, and about 0·2 to 0·1 m.m. in diameter. Prof. Schuster naturally assumes that these spherical particles have been derived from the fused surfaces of meteorites in their passage through the atmosphere. He accounts for their non-oxidised condition partly by the fact that nickel iron alloys are less readily oxidised than iron, also that the fusion and separation from the meteorites probably took place in the upper regions of the atmosphere where the amount of oxygen is exceedingly small; at a height of only 200 kilometres the percentage of oxygen in the air is only about 0·8. He then refers to the presence of an unknown gas in the atmosphere indicated by a green line shown in the Aurora borealis spectrum—he assumes that this gas must have a very low density; supposing that it be as light as hydrogen, and that at the surface of the earth its quantity per cubic centimetre is only the one millionth part of the oxygen present in the same space, it would certainly escape all our methods of analysis. (1882). At a height of 200 kilometres it must exceed the oxygen in the proportion of 170,000 to 1; that is to say, at that height the atmosphere would practically contain no oxygen. . . . Even if there are only minute quantities of free hydrogen on the surface of the earth, it may be in preponderating proportion in the upper regions.

Tissandier has shown how by burning iron wire in oxygen, we may often obtain iron spherules of exactly the same nature as those floating in our atmosphere.

"I have obtained similar spherules by using an iron file

as one pole of a dynamo machine, and passing the file over a copper wire connected with the other pole. The sparks consist chiefly of iron globules like those to which Tissandier attributes a meteoric origin; there are also spongy metallic masses, which present exactly the same appearance as the metallic iron found in the Sahara desert. The reason why they did not oxidise is no doubt due to the fact that a layer which were oxidised used up the oxygen in the neighbourhood of the few particles which escaped."

In 1883, the above Committee reported that three specimens of solid matter from snow and ice of the Himalayas were collected and examined. One from the Gamukdori Pass (lat. 35° 5′, long. 74° 13′) 13,400 ft., and two from the Shokari Pass (lat. 35°, long. 74° 38′) 14,700 ft. There is no human habitation near either of these places. The residue amounted to 0·1 grm. for the 25 cubic feet of snow boiled down in each case. All three specimens contained (1) spherical particles of magnetic oxide of iron, (2) small particles of metallic iron. These probably are of meteoric origin.

From the foregoing evidence, it is extremely probable that, as suggested by Haidinger, Reichenbach, and others, at all times and in all parts of the world there is a constant although imperceptible rain of such meteoric dust gently descending upon the earth's surface, the amount undergoing considerable variation, at times being much greater than at others, and from all accounts the fall in the month of November is the most abundant. This meteoric dust is apparently of the same general nature, and is probably derived from the same sources as the larger masses known as meteorites.

Roof dust, collected from the beams under the roof of the University, February 24, 1882. The proportion of magnetic material separated from one lot of this dust was 1·3 per cent, another lot gave 1·7 per cent. Most of it acquired a metallic lustre when ground in the mortar; some of this was fused with caustic soda, and the metallic residue was found to contain cobalt and nickel.

Mud from a Cistern.—Collected March 3, 1882, from a rain-water cistern (open) under the roof of the University building. When dried it yielded a grey coloured powder, containing sand grains, vegetable fibres, &c. The magnetic portion was fused with caustic soda to separate the iron oxides and entangled matters; the metallic portion contained traces of cobalt, but the indications for nickel were not satisfactory. The cobalt was present in less quantity in this than in the other roof dusts.

(To be continued).

PROCEEDINGS OF SOCIETIES.

THE FARADAY SOCIETY.

The Faraday Society, whose membership roll now numbers some 240 strong, held its first meeting on Tuesday evening, June 30th, at the Rooms of the Chemical Society, Burlington House, W., in the presence of a considerable audience. The President, Dr. J. W. Swan, F.R.S., was unfortunately unable to be present, so the chair was taken by Mr. J. Swinburne, one of the Vice-Presidents.

The formal business of adopting the Rules that had been drawn up by the Council having been been disposed of, the Chairman read a short Introductory Address by Dr. Swan, in which he drew attention to the purpose and necessity of the Society. Dr. Swan's address will be printed in full in the *Proceedings* of the Society.

Mr. W. C. Dampier Whetham, F.R.S., then gave an abstract of his paper on "*The Present Position of the Theory of Electrolysis.*"

The fact that the products of electrolysis appeared at the electrodes only led to the Grotthus chain hypothesis. Faraday's laws suggest opposite convective streams of anions and cations. Hittorf's observations on the unequal concentration of the solution lead to the conception either of complex ions, dragging along salt or solution, or else unequal velocities of the ions, whose ratio can be measured. Kohlrausch's measurements of the resistance of electrolytes enable the absolute velocities to be measured. The fact that the conduction of electricity in solutions obeys Ohm's law shows that the E.M.F. is merely directive, and that the ions have migratory freedom. The fact that ionic mobilities only vary slowly with dilution, while the conductivity of a dilute solution is proportional to the first power and not to the cube of the concentration, shows that the ions must be free of the solute molecules—not necessarily of those of the solvent. The osmotic properties of electrolytes lead to the same conclusion. A short consideration of conduction in non-aqueous solutions and in fused electrolytes completes the paper.

In the discussion which followed, Dr. R. A. Lehfeldt drew attention to the work of Jahn and Nernst on strong solutions.

Dr. T. M. Lowry discussed the question of conduction in the Nernst filament, which he regarded as a mixture of electrolytes.

The Secretary read communications from Dr. Swan and Prof. Armstrong. The latter severely criticised the Dissociation Theory as involving necessary assumptions not in harmony with known facts. He hoped the Faraday Society would take no hasty decisions, but from the outset act with true scientific caution, and he applied for a fuller and more scientific use of the imagination in dealing with the phenomena underlying electrolysis.

In replying to some of Prof. Armstrong's strictures, Mr. Whetham remarked that although the early dissociationists unduly neglected the action of the solvent, that was by no means at present. "Free" ions means free from one another, not free from molecules of the solvent, and it is no part of the Dissociation Theory to deny that ions may be linked to the solvent, there being processes of interchanges allowing the ions to work their way through the solution.

Mr. James Swinburne followed with a short account of his paper on "*Chlorine Smelting with Electrolysis*," The process, which is an entirely new departure in the metallurgy of complex sulphide ores, consists, briefly, in treating the ores with hot chlorine, the temperature being of prime importance. This drives off pure sulphur. The mixed chlorides are then chemically treated by substitution, so that ultimately all the chlorine is combined with zinc, and, finally, the fused zinc chloride is electrolysed. The process is thus perfectly cyclical. Full figures of costs are given.

Mr. Bertram Blount, who had seen the process at work, looked forward with confidence to the time when it would be applied on a large scale, yielding handsome profits.

Dr. O. J. Steinhart, in the course of an interesting speech, asked for particulars regarding the losses of chlorine and metals.

Mr. R. S. Hutton remarked that if the process could be applied to such ores as the Sudbury nickel ores, it should prove of great value.

Mr. Swinburne, in his reply, stated that very little chlorine was wasted, while there was practically no point where loss of metal was possible. The difficulty as regards consumption of electrodes was got over by using cheap carbon in a preliminary electrolysis, until the fused zinc chloride was practically anhydrous.

Dr. Lehfeldt's paper on "*The Total and Free Energy of the Lead Accumulator*" was taken as read, and the discussion adjourned until the next meeting.

Dr. F. M. Perkin exhibited and explained some novel forms of Electrodes for Electrolytic Analyses.

Change of Address.—We understand that, owing to the rapid increase of their business, Messrs. Geipel & Lange are removing to new and more commodious premises at 72a, St. Thomas Street, S.E., where they have also obtained a large warehouse for the purpose of increasing their stock of electrical apparatus of the descriptions which they are known to deal in.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 24, June 15, 1903.

Crystallisation of Slightly Soluble Bodies.—A. de Schulten.—The method of slow diffusion by which a number of crystalline bodies can be prepared can only be employed at ordinary temperatures. The author modifies this method so that it can be used where higher temperatures are necessary. For example, a solution of barium chloride and strong hydrochloric acid is placed in a flask heated on a water-bath, and sulphuric acid slowly dropped in, thorough mixing being insured by the convection currents from the water-bath. At the end of twenty-four hours crystals of barium sulphate begin to appear, and at the end of one month crystals of a measurable size can be collected. The same method can be employed for the preparation of celestine and anglesite.

Substitution of Zinc for Lead in Pigments.—T. L. Breton.—The author satisfactorily demonstrates that fresh paints containing lead do give off plumbic emanations, which may have grave effects on the health of those persons breathing them. He believes that from a hygienic point of view zinc paints should in all possible cases be substituted for lead.

Colloidal Silver.—M. Hanriot.—In a previous research the author showed that the commercial product known as collargol is not an allotropic modification of silver, but an alkaline salt of a true acid, collargolic acid. On seeking to purify this product by means of dilute acetic acid and ammonia, lysalbinic acid remains in the mother-liquor. After four precipitations the proportion of the two substances becomes constant, silver 93·1 per cent and lysalbine 6·1 per cent. The author also investigates the properties of this body.

Fusibility of Mixtures of Antimony Sulphide and Silver Sulphide.—H. Pélabon.—The curve of fusibility of mixtures of silver and antimony sulphides can be accurately constructed. It presents two maximum ordinates, which indicate the existence of two definite compounds, $Sb_2S_3.Ag_2S$ and $Sb_2S_3.3Ag_2S$. It also presents three minimum ordinates differing very slightly from one another which correspond to three different eutectic mixtures.

Etherification of Sulphuric Acid.—A. Villiers.—The author performs experiments on the rate of etherification of sulphuric acid. Analyses were made of mixtures prepared in 1878, preserved in sealed bulbs at ordinary temperatures. His experiments seem to show that the limit of etherification, obtained by the action of alcohol on sulphuric acid, is the same whatever the temperature.

Certain Derivatives of Aminopyromucic Acid and Furfuranamine.—R. Marquis.—Nitropyromucic acid, when reduced by means of tin and hydrochloric acid, forms only succinic acid, carbonic acid, and ammonia. The author further investigates the reduction products of this substance, and obtains an amine derivative by the action of aluminium amalgam. He also prepares and examines the properties of ethyl aminopyromucate, $C_4H_2O{<}^{NH_2}_{CO_2C_2H_5}$, ethyl acetaminopyromucate, $C_4H_2O{<}^{NH—CO—CH_3}_{CO_2C_2H_5}$, ethyl benzoylaminopyromucate, acetaminopyromucic acid, $C_4H_2O{<}^{NH.CO.CH_3}_{CO_2H}$, and acetyl furfuranamine, $C_4H_3O—NH—CO.CH_3$.

Action of Phosphorus Trichloride on Glycerin.—P. Carré.—Phosphorus trichloride behaves with glycerin in the same way as with glycol. A phosphorous ether of glycerin, $P_2O_6(C_3H_5)_2$, is produced, and a phosphorous ether of monochlorhydrine and glycerin, $P.OH.O_2C_3H_5Cl$; these are immediately decomposed by cold water, giving the compounds $P_2(OH)_4O_2C_3H_5OH$ and $P(OH)_2O.C_3H_5.OHCl$, isolated in the form of their calcium salts. The action of phosphorus trichloride on glycol and glycerin results in the formation of ethers containing 2 mols. of phosphorous acid for 1 mol. of polyatomic alcohol, whilst the direct reaction of the acid on these alcohols only causes the fixation of a single molecule of the acid on to 1 mol. of glycol or glycerin.

Action of Sulphuretted Hydrogen on Methylethylketone (Butanone).—F. Leteur.—When hydrogen sulphide reacts on a solution of ordinary acetone in strong hydrochloric acid at low temperatures the oxygen is replaced by sulphur and a substance called trithioacetone produced. The author modifies this method to render it applicable to butanethione for the following reasons:—(1) The presence of a certain quantity of water affects the reaction; (2) ketones being susceptible to alterations under the influence of hydrochloric acid, the products of their decomposition enter into the reaction. To avoid these two sources of error the author performs his experiments at a very low temperature and in the absence of water.

Two Isomeric Carbides of Campholene and Camphene.—L. Bouveault and G. Blanc.—The authors prepare carbides containing the group $=CH_2$ in order to compare their properties with those of the known carbides, campholene and camphene.

Synthesis of 2.2-Dimethylglutaric Acid.—E. E. Blaise.—Unsuitable for abstraction.

Atmospheric Formic Acid.—H. Henriet.—In a previous research the author showed the apparent existence in the air of a gaseous body formed by the union of a nitrogen base and an acid, probably formic acid. By a series of experiments described in this paper he completely identifies this to be formic acid.

Properties of Phenylglycolic Acid.—Œchsner de Coninck.—When phenylglycolic acid is heated in presence of an excess of sulphuric acid or glycerin small quantities of carbonic anhydride are produced. The author investigates the mechanism of this reaction, and during this research discovers new properties of phenylglycolic acid.

The St. Louis Exhibition, 1904.—The Royal Commission for the St. Louis Exhibition, 1904, is specially desirous of securing a series of collective exhibits adequately representing the chemical industries of this country, and a sub-committee has been appointed to carry out the necessary arrangements. It is well known that other nations have already made provision for similar exhibits, and it would be most regrettable if Great Britain were placed in a less favourable position through the abstention of important members of the trade. No doubt in the circumstances of the case the benefits which manufacturers may be expected to derive from participation are mainly indirect, and it is perhaps necessary to appeal rather to patriotism than to business instincts in securing support, but it is gratifying to find so many of the leading firms of chemical manufacturers have already signified their willingness to exhibit, that a successful result may be regarded as already assured; much, however, yet remains to be done in this direction. For collective exhibits the Commission will, in addition to providing free space, make such arrangements as will largely reduce the expenses which exhibitors are ordinarily called upon to bear. Particulars of the course proposed to be adopted in carrying this into effect can be obtained from the Secretary of the Liberal Arts Committee, at the office of the Royal Commission for the St. Louis Exhibition, 1904, 47, Victoria Street, Westminster, S.W., and as it is needful that the Commission should as soon as possible be placed in a position to indicate the amount of space which will be required, it is hoped that those who have not already signified their intention to take part in the Exhibition will do so promptly.

Erartum.—P. 16, col. 1, *for* "John McDonald" *read* "John McDowall."

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Prospectuses on application to the SECRETARY.

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2278.

ON THE SCINTILLATING PHOSPHORESCENCE OF SIDOT'S BLENDE CAUSED BY RADIO-ACTIVE EMANATION.

By J. ELSTER and H. GEITEL.

Some days ago there appeared in an English daily paper (*Westminster Gazette* of March 20, 1903) a report of a paper read before the Royal Society by Sir William Crookes, on March 19th, entitled "The Emanations of Radium," which related to the peculiar kind of phosphorescence caused by the emanation of radio-active substances on a screen of Sidot's blende. Some time ago we noticed the phenomenon described by Crookes in the course of experiments which we had performed for the purpose of producing distinct phosphorescence by means of the active emanation contained in the air of the ground, and we meant to describe them very soon in a complete report on the results of further investigations of the activity of the air of the ground. As an addition to the above mentioned notice the following description of our experiments may now be of interest.

If we introduced into a dark space of about 1½ cubic metres capacity, which contained the radio-active emanation of the ground, an insulated screen of Sidot's blende, which had been kept in the dark for some days previously, and maintained it for about two hours at a negative potential of 2000 volts, it became luminous. On examining the screen more closely in the dark with a thoroughly well rested eye, we discovered the striking fact that the screen was not uniformly illuminated, but that the intensity of the light of the individual parts of the luminous surface was subjected to a constant change. If a screen thus rendered luminous is observed through a microscope it is seen that the scintillating of the screen is due to a number of separate luminous specks, each of which only flashes out momentarily.

As Crookes explained in the description of his experiment, when the luminous surface was examined by means of a magnifying glass, the effect was that of looking through a telescope at a group of stars, each of which flashed out only to disappear again at once in the black background.

As we have not for years had any radio-active substance in our laboratory because of our researches on the radio-activity of natural air, we have not been able to examine more closely the phenomenon in the case of strongly active substances, but we also obtained it, and indeed more clearly, with the air of the ground in a room situated at some distance from our laboratory, within a space of about 40 litres capacity, impregnated with thorium hydroxide (50 grms.). Finally, Giesel was kind enough to place at our disposal in his house all the emanating substance he had for the purpose of research.

On using the "emanation substance" (*cf.*, F. Giesel, *Ber. d. Deutsch. Chem. Gesell.*, 1903, xxxvi., p. 342) the scintillating luminosity of the screen was also visible in an incompletely darkened space, and the aspect which the screen presented through a microscope was even more surprising; it could also be easily shown that this phosphorescent light is *not* extinguished by the influence of red light. This is a characteristic and easily understood difference between the phosphorescence produced by emanation and that produced by illumination. If the emanation substance wrapped in paper was laid directly on the (unelectric) screen, the latter showed the same scintillating phosphorescence. A luminous screen of calcium tungstate after an exposure of about one hour was rendered lastingly luminous, but the characteristic scintillating of zinc blende was not visible.

It must be mentioned that in the space prepared with thorium oxide the scintillating luminosity of the blende would be obtained, if with somewhat less intensity, after positive electrification. We have not carried out analogous experiments with the emanation substance.

In order to prove whether the flashing of the luminous points proceeded from little fragments of the active emanation which adhered to the screen itself, or from those fragments which had loosened themselves, and which radiated back on to the screen, we led a current of air over the screen. With the small speeds we employed no effect of the movement of the air was noticed. Moreover, the phenomenon remained the same whether the screen was closely pressed with its luminous side against a glass plate or not. This result would be compatible with the opinion expressed by Crookes, that the flashes of light are directly connected with the hurling off of electrons by the active surface itself. It would then appear remarkable that the screen of calcium tungstate did not exhibit the phenomenon. —*Physikalische Zeitschrift*, iv., 15, 439.

Wolfenbüttel, March 27, 1903.

COLOURED REACTIONS OF CHLOROFORM, BROMOFORM, AND IODOFORM.

By R. DUPOUY.

When we react with chloroform on the phenols in the presence of dry potash, we obtain very brilliant colourations, very probably due to the formation of colouring matters belonging to the aurin group.

In this manner, with ordinary phenol we obtain a yellow colouration, with resorcin a bright red, and with naphthol a blue colouration.

I have tried this reaction with most of the phenols, and I have observed that by using isopropylmethylphenol or thymol, and by reacting with sulphuric acid on the product first formed, in the presence of potash, it was possible to obtain new colouring matters having characteristic absorption spectra. The following is the most convenient manner of proceeding :—

We place half a cubic centimetre of an alcoholic solution of thymol at 5 per cent in a test-tube; add a drop or chloroform and a morsel of caustic potash. This must be heated and kept at the boiling point for about half a minute. We then notice that the mixture has become yellow in colour, with a more or less pronounced reddish tint, according to the amount of chloroform used. Then we add, very carefully, a cubic centimetre of sulphuric acid, and again heat to boiling. A magnificent violet colour is then obtained, which is generally too intense to allow of direct examination with the spectroscope.

Therefore, a few drops of the violet liquid are poured into a little acetic acid, and a spectroscopic examination made, when we observe a spectrum which may be best compared with that of oxyhæmoglobin, characterised, as we know, by two bands situated in the green. However, this absorption spectrum differs a little from that of oxyhæmoglobin, as it is nearer the red end of the spectrum.

If instead of pouring the violet solution into acetic acid, we mix a few drops with water, we obtain a blue liquid, which gives a spectrum characterised by a band situated between the D line and the red.

As can be seen, this reaction differs completely from that which has been described by Vitali, and which consists of the use of a mixture of potash and thymol, which, under the influence of chloroform vapour, takes a violet colour.

Further, very small quantities of chloroform can be detected by means of this reaction, and for toxicological research we may use Vitali's apparatus, and, as recommended by the author (*Gazzetta Chimica Italiana*, 1881,

p. 489), draw in the chloroform in a stream of hydrogen for example. By letting the gas bubble through one cubic centimetre of an alcoholic solution of thymol, and proceeding as described above, we obtain a more or less intense violet colouration.

We may remark here, that in the absence of chloroform, sulphuric acid will occasionally give a very faint bluish colouration with thymol and potash, but the solution is entirely without spectral reactions. Further, to avoid all error, the sulphuric acid must be added only after the yellow colour has been first observed, and if this does not occur, it is useless to go on with the experiment.

Again, I have satisfied myself that all the coloured reactions of chloroform, which are described as characteristic in most treatises on analytical chemistry, succeed equally well with bromoform, and sometimes also with iodoform. In fact, the reaction I have just described can be obtained easily with bromoform, but more difficultly with iodoform. This circumstance must be borne in mind in the toxicological search for the trihalogen derivatives of methane.—*Bull. de la Société de Pharmacie de Bordeaux*, May, 1903, p. 140.

THE ELECTROLYTIC MANUFACTURE OF VANADIUM AND ITS ALLOYS.*

By GUSTAVE GIN.

The principle of my process depends on the high conductivity of the trioxide of vanadium, and on the facility with which the trifluoride of vanadium is obtained, on attacking the trioxide with fluorine in the presence of carbon.

To illustrate how these characteristic properties can be utilised, let us suppose that we are electrolysing ferrous fluoride in solution, in fused fluoride of calcium, using an anode formed of an intimately agglomerated mixture of trioxide of vanadium and carbon, the cathode consisting of a bath of metallic iron.

The ferrous fluoride being decomposed by the current, the fluorine given off at the anode attacks the trioxide of vanadium, which gives up its oxygen to the carbon, while trifluoride of vanadium is formed according to the reaction $6F + V_2O_3 + 3C = 2VF_3 + 3CO$. The fluoride of vanadium formed goes into solution in the fluoride of calcium, and is electrolysed in its turn :—

$$2VF_3 = \overline{\boxed{2V}}^{-} + \overline{\boxed{6F}}^{+}$$

The vanadium set at liberty combines with the metallic iron of the cathode, and at the anode there forms a fresh quantity of fluoride of vanadium, which is again electrolysed, so that the ferrous fluoride in question only serves to start the operation, furnishing the fluorine which acts as a vehicle for the vanadium to pass from the anode to the cathode.

I will now explain how I proceed in practice. Trioxide of vanadium, prepared by the calcination of vanadic acid in the presence of carbon, is mixed with a suitable proportion of retort carbon and powdered resin, so as to obtain a homogeneous, plastic paste by hot kneading. After being agglomerated in a special kneading trough, heated from the exterior, the paste passes to a mill, where it is crushed by heavy steel rolls. The paste leaving the mill is pounded, then by hydraulic pressure forced through a die similar to those used in the manufacture of electric light carbons. Finally we obtain prismatic or cylindrical rods, which are baked, in the absence of air, in very hot ovens.

Electrodes manufactured in this manner are kept protected from the air and moisture under a layer of some dry pulverulent substance, until they are required for use. I devised this means for the manufacture of these electrodes in conjunction with Dr. Gans, who supplied me with the vanadic acid necessary for my experiments.

The specific resistance of these electrodes was measured in the Laboratoire Central d'Electricité, at Paris, with the help of MM. Chaumat, Delon, and Petitalot, and was found to be 13.700 microhm-centimetres, at a temperature of 15° C. Electrodes made in the manner just described appear to be able to carry a current equal to 7/10ths of that used with carbon electrodes of the same sectional area.

The anode in my furnace consists of a bundle of electrodes made in the above manner; the cathode is formed of a block of steel. Certain special arrangements are necessary on account of the high fusing point of vanadium, and of the alloys containing it in any considerable quantity. For alloys with more than 25 per cent of vanadium, the cathodic section should be considerably less than the active surface of the anodes. A good return and a sufficiently fluid bath are obtained with a mean current density of 2 ampères per square centimetre of section of the anode, and 6 ampères per square centimetre of cathode, the electromotive force being from 11 to 12 volts.

As I observed at the commencement, the ferrous fluoride introduced into the bath at the beginning of the operation is only for the purpose of starting the electrolysis. Nevertheless, as a certain quantity of fluorine is lost by being transformed into gaseous tetrafluoride of carbon, on contact with the excess of carbon in the mixture forming the anode, it is advisable to compensate for this loss by adding a certain amount of ferrous fluoride from time to time.

The iron constituting the bath is added in the metallic state, by small quantities at a time, after each pouring of the ferro-vanadium. If no iron were added to the bath, we might obtain almost pure vanadium, but the casting of this substance is extremely difficult, and it must be taken from the furnace in the solid form, It is apparent that my process is applicable, under similar conditions, to the commercial manufacture of alloys of vanadium with other metals, such as copper, aluminium, manganese, &c. It suffices to replace the cathodic bath of iron by one of the metal it is wished to introduce into the alloy.

* A Paper read before Section X., at the Fifth International Chemical Congress at Berlin.

SOME PROPERTIES OF COLLOIDAL SILVER.

By A. CHASSEVANT and S. POSTERNAK.

Colloidal silver is at present the object of numerous researches, on account of its recent therapeutic applications both in France and in other countries. At the last meeting of the Société Chimique, M. Hanriot made an interesting communication on Heyden's commercial collargol, which he looks upon as the ammoniacal salt of a definite acid, collargolic acid. One of us who was present at that meeting announced that we had prepared colloidal silver by a method analogous to that of Carey Lea, and that we were following up the examination of its chemical and physical properties.

For the purpose of preparing this colloidal silver, we followed the method adopted by Carey Lea for citrate of iron, with some modifications which gave us a much better return in its production. In this manner we obtained an amorphous product of a greyish metallic appearance with some iridescence.

This product, almost insoluble in water, dissolves to a very great extent in ammonia, giving it a deep brownish colouration.

It contains 90·08 per cent of silver, and a little iron and citric acid; it does not contain any albuminoid matter.

The properties of this compound are as follows :—

It is soluble in ammonia and in the alkalis; it is pre-

cipitated from its solutions when we add a dilute acid in suitable proportion.

Its ammoniacal solution, poured into an excess of dilute acetic acid, gives an acid solution of a brown colour, retaining all the properties of colloidal silver, and does not become cloudy until after several hours. Nitric acid in excess decolourises it.

Carbonate of soda and carbonate of ammonia precipitate colloidal silver completely from its solutions.

Baryta water also causes complete precipitation.

Soda and ammonia in excess do not give any precipitate; but when these solutions are left exposed to the air, the carbonation of the alkalis causes the complete precipitation of the colloidal silver.

Sulphate of copper, when added in suitable proportion, precipitates the whole of the silver.

If we proceed comparatively with solutions containing the same amount of colloidal silver, but increasing amounts of ammonia, we observe that it is necessary to add increasing amounts of sulphate of copper in order to obtain the complete precipitation of the colloidal silver.

It appears to be necessary to add sufficient copper to saturate almost the whole of the ammonia present. The precipitate consists of a mixture of silver and hydrate of copper.

With nitrate of silver, sulphate of nickel, &c., we obtain analogous results.

We must not overlook a very curious property that has been already described. The more this product is triturated in an agate mortar, the less soluble it becomes in its solvents. A comparative experiment with a solution of ammonia containing 0·015 per cent of ammonia, with the initial product, and with the product ground for five minutes, gave different results. The first solution is of a deep brown colour, and contains a great deal of silver; the other is a bright yellow, and contains only a little silver but a good deal of impurities. It seems as if this mechanical action has changed the colloidal product to metallic silver, and has set free the impurities adhering to the physical particles of the colloidal silver.

The electrolytic phenomena are different, according to whether we pass the current through an alkaline or an acid solution of colloidal silver.

In the first case, we have observed that the colloidal silver is transformed towards the positive pole or anode, and that the brownish deposit which appears on the electrode re-dissolves in the ammoniacal water, giving a brownish solution.

When, on the other hand, we pass an electric current through an acetic solution of colloidal silver, the deposit occurs on the negative or cathode pole. It might be objected that the acetic acid has transformed the colloidal silver into acetate of silver, and that it is the basic silver that is deposited. Such, however, is not the case. The deposit on the platinum cathode is of a brown colour, and with dilute ammonia gives a brownish solution identical with the original one.

These phenomena of the transference of the physical particles which occurs alternatively at the positive or anode pole in the case of an alkaline solution, and at the negative or cathode pole in the case of an acid solution, are analogous with the facts already observed by other writers with other colloidal substances, facts already published by one of us (Posternak, *Ann. de l'Institut Pasteur*, 1901, p. 400, and Erratum, p. 451).

In our experiment with the electric current, colloidal silver behaves in the same manner as the flocks of albumin in Hardy's experiments (Hardy, *Zeit. Physik. Ch.*, vol. xxx., p. 285), and the flocks of hydrate of iron, silica, &c., in the experiments of Lindeer and Picton (*Chem. Soc.*, 1897, vol. lxxi., p. 568). We must admit, therefore, that the different direction given by the electric current to the physical particles of colloidal silver in acid or alkaline solution, is not due to the chemical properties of this body, but to the electrostatic charges communicated to its particles by the most mobile *ions* present in these solutions. A positive charge in the case of acid liquids (the most mobile ion being H^+), and a negative charge in the case of alkaline solutions (the most mobile ion being OH^-).

These facts have been demonstrated already by Posternak in the case of colloids, and have just recently received confirmation in a research by Knoblauch.

The summary of the reactions we have just described enables us to state that the product we have prepared possesses the properties of a colloid, and that a definite chemical function cannot be attributed to it, since we know that the solubility of colloids in acids and alkalis does not suffice for us to affirm the basic or acid nature of their functions.

If we admitted that colloidal silver was an acid, because of its solubility in ammonia and in the alkalis, it would be necessary also to admit that it is a base because of its solubility in acetic acid.

It is difficult to comprehend how the ammoniacal salt of colloidal silver, soluble in water, could be precipitated by carbonate of ammonia or carbonate of soda; and again, why in acetic solution the radical with an acid function (colloidal silver) of the ammoniacal salt goes to the negative pole, which is contrary to what we know of the electrolysis of salts in acid solution.

It must be well understood that all the above facts apply only to the product we have prepared; it would be interesting to compare this colloidal silver with commercial collargol, which, among other impurities, contains an albuminoid substance which may mask or modify the reactions of the mineral colloid.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 11.

RADIUM AND HELIUM.

The following paragraph appeared in *The Times* of the 20th inst:—

"A paper bearing in a remarkable way on the connection between these two elements, which is now exciting so much interest, has been received for publication by the Royal Society from Sir W. and Lady Huggins. Prompted, in fact, by theoretical ideas, they attacked the problem of the spectroscopic analysis of the light emitted directly by a radium salt at ordinary temperatures. Preliminary visual observation seemed to show traces of bright lines in a continuous spectrum. Preparations were accordingly made for photographic record by means of a small quartz spectroscope constructed some years ago for use on very faint celestial objects. After several trials, a spectrum consisting of eight definite bright lines in the ultra-violet, entirely different from the spark spectrum of radium, and some faint lines together with a very faint continuous spectrum, was obtained by seventy-two hours' exposure to the glow. The lines were of some breadth, on account of the wide slit that had to be employed in order to admit sufficient light; but it was found possible to measure their wave-lengths within an error of two in the fourth figure. On a comparison of this spectrum, so different in type from an ordinary phosphorescent spectrum, with the recorded measurements for helium, it appeared at once that four, and perhaps five, of the eight lines agreed with lines of helium within the uncertainty of the measurements. Another line, that of highest refrangibility, agrees with a line in the spark spectrum of radium itself, which, however, has not been recorded by other observers; the two other lines, the lowest, have not yet been traced.

"It will be remembered that last year Prof. Rutherford produced striking evidence for the view that, in the very slow break-up of radium that is concomitant with its radio-activity, the inert gas helium is one of the products formed. Recently, Sir W. Ramsay and Mr. F. Soddy have succeeded in detecting helium by the spectroscope in the

gases extracted from a radium salt. If, as the present observations indicate, the radium salt shines spontaneously in the dark largely by light belonging to the different element helium, another important step is gained in elucidating the nature of the instability of such chemical elements of high atomic weight and the radio-activity associated with it."

Speaking at the Dinner of the Society of Chemical Industry at Bradford, on the 16th inst., Sir William Ramsay, President, described a new development of the radium mystery.

For some time (he said) two very distinguished young scientists belonging to Canada—Prof. Rutherford, of Montreal, and Mr. Soddy, who was now working in his laboratory—had been investigating the properties of those mysterious elements which had the power of discharging an electroscope when they were brought near it. His audience were aware, no doubt, that that property was first discovered for uranium by M. Becquerel, of Paris, and not long afterwards Mdme. Curie discovered the wonderful element, radium. Messrs. Rutherford and Soddy discovered that thorium, an element not far removed from radium and uranium, gave off what they called an emanation, or what might might be called a gas—a substance that could be moved from place to place, which could be condensed by cooling at a sufficiently low temperature, but which was most remarkable as a substance which discharged a loaded electroscope, and also as a substance which shone in the dark. They pointed out that radium gave out a similar emanation or gas continuously, that any salt of radium—radium bromide was what was generally used—but any salt of radium if allowed to stand for a while accumulated a further quantity of gas which could be removed with a pump or by washing it out with another gas. This very curious substance lost its properties on standing. If it was allowed to remain for four days it had parted with half its power to discharge an electroscope, and became, if looked at in the dark—as far as one could judge by the eye—half as luminous. And as time went on it lost its power of discharging electricity, and also its luminosity, until at length there was nothing left. There appeared to be no residue as far as one could tell. Mr. Soddy had done him the honour of coming and working in his laboratory, and as he (the speaker) had had some little experience in dealing with small quantities of gas, they laid their heads together, and had contrived to examine this emanation or gas given off by radium. He might tell those who did not know, that radium was very expensive, because it was a very rare substance, and that £25 would buy a very small quantity indeed—less than one grain. They managed to scrape together the needful, and invested in as much radium as they could get—all that there was in the market at the present moment.

Having examined this gas (Sir William continued) we found, to our astonishment, the other day that the emanation contains a quantity of helium, a light constituent of the atmosphere. I don't wish to imply that the emanation is helium, for it is not. The gas was first passed through a tube cooled with liquid air, in which the emanation stays behind, being condensed at that low temperature. But the other gas passes through this cold tube, and when collected in a microscopic Pluecker tube—what we call a vacuum tube—it shows undoubtedly the whole spectrum of helium (applause). It is impossible to forecast what this implies, but you must remember that the radium bromide which we have obtained, prepared, no doubt, by the same process which the Curies used, namely, the decomposition of pitchblende, a uranium mineral, with precipitation of barium by means of sulphuric acid, and with it radium, and separation of radium from barium by fractional crystallisation—that this radium obtained from pitchblende can hardly be supposed to have retained any helium through all those manifold operations. And it would follow that the helium must be generated from the radium or from the gas—the emanation—which the radium gives off. At present I am as much in the dark about it as anyone. I merely chronicle the fact that there is undoubtedly a production of helium continuously from radium.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending June 30th, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Charles Perrin, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, July 9th, 1903.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 203 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 2nd to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 203 samples examined by us during the month, 198 were found to be clear, bright, and well filtered; four samples were recorded as clear but dull, and one was very slightly turbid.

The rainfall at Oxford during June has been remarkable in more ways than one; the actual amount of rain measured was 5·58 inches, a larger amount than we have ever recorded before in one month, but this rain fell on ten days only, and by far the greater portion of it between the 8th and the 16th inst., and no rain fell at all after the 19th. The average fall for the month is 2·10 inches, so we have an excess for June of 3·48 inches, which added to the previous one of 4·35 inches, gives a total excess for the first half of the year of 7·83 inches, or 72·4 per cent on the thirty-five years' average.

Last month the total excess of rainfall amounted to 49·9 per cent on the thirty years' average, so that during the month of June actually 22·5 per cent, or an amount approaching one-half of the previous excess of rain, has fallen in the valley of the Thames. Such an amount of rain is altogether exceptional in our twenty-two years' experience. The result has been that, as we pointed out in our report for May, the proportion of vegetable matter in solution, and therefore the colour of the water, are both quite exceptional for the summer months. Nevertheless, the general filtration has been adequately and effectively performed, as is shown by the following bacteriological results. (See next column).

Of the 269 daily samples taken from the filter wells of the Metropolitan Water Companies, twelve samples, or 4·4 per cent were sterile. There were fifteen samples, or 5·5 per cent, containing more than 100 microbes, and of these, eight samples contained more than 150 microbes per c.c. The fifteen excess samples contained an average of 247 microbes per c.c.: in May seven excess samples contained an average of 124.

Our bacteriological examinations of 342 samples taken during the last month have given the results recorded in the following table. Besides these samples we have examined 243 others from special wells, standpipes, &c., making a total of 585 samples in all :—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	151
New River, filtered (mean of 69 samples) ..	7
Thames, unfiltered (mean of 23 samples).. ..	10337
Thames-derived water from the clear-water wells of seven Thames-derived supplies (mean of 175 samples)	42
Ditto ditto .. .. highest	588
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 25 samples) ..	474
River Lea, from the East London Water Company's clear-water wells (mean of 25 samples)	28

Although therefore the mean number of microbes in the filtered supply is higher than in May, the increment is not excessive, and moreover was not generally distributed over the whole area of supply.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

METEORIC DUSTS, NEW SOUTH WALES.*

By Prof. A. LIVERSIDGE, LL.D., F.R.S., University of Sydney.

(Continued from p. 34).

Roof Dust.—In March, 1882, Mr. Russell, Government Astronomer, collected for me some dust from the roof of the Sydney Observatory. From 493 grms. of this the magnet extracted 48·5 grms., or roughly 9·8 per cent; but as this evidently contained much entangled non-magnetic matter, it was boiled with caustic soda and repeatedly extracted with a magnet under the soda solution. The proportion of magnetic matter to the original dust was then found to be only 1·5 per cent. Under the microscope it had the appearance of Fe_3O_4, but with it were some lustrous steely looking flakes. The magnetic material was found to contain both cobalt and nickel.

The comparatively large quantity of magnetic matter in the three Sydney dusts is probably due to the lighter materials having been gradually removed; *i.e.*, the two dusts had been subjected to a process of vanning by air currents, and the mud had been concentrated by the water flowing in and out of the cistern.

These dusts collected in Sydney confirm the results obtained by M. Tissandier and others; it was thought sufficient to ascertain the presence of cobalt and nickel. The quantitative analyses were not undertaken, as they would have occupied a great deal of time, and would have afforded but very little more information.

Meteoric Dust from Uralla, collected by Mr. Cleghorne, December 14, 1883. A fine reddish dust with some angular grains; most are clear and colourless, but some are yellow or red. Like the other red dusts, it contains granules of concretionary calcium carbonate, which dissolve with effervescence in acetic acid, also particles of charcoal or decayed vegetable matter. The average size of the grains is from 0·01 to 0·02 m.m.

Analysis.

Moisture at 100°	4·25
Silica	70·60
Iron sesquioxide	4·66
Alumina..	18·74
Lime	0·70
Undetermined	1·05
	100·00

* Read before the Royal Society of N.S. Wales, September 3, 1902. From the *Journal and Proceedings of the Royal Society of N.S. Wales*, vol. xxxvi., p. 241.

Mr. Cleghorne, in writing from Uralla, on December 14, 1883, says: "I enclose herewith a sample of dust which fell in this neighbourhood yesterday (Thursday) morning. About 5 o'clock on Wednesday evening we had a sudden and severe thunder-storm, with much rain and some hail; the evening was clear moonlight, but during the night we had several thunder showers, especially towards morning —from early morning to about 11 a.m. there was a very singular yellow coloured fog, all vegetation was sprinkled with fine yellow dust, it could be easily gathered from iron roofs, but it appears to have fallen before the showers of rain in the morning, as it had been washed into the gutters of the roofing, and partially washed from the leaves, some samples of which I also enclose. I have not yet been able to learn how far this unusual occurrence extended."

The foregoing part of this paper, except the quantitative analyses, was written about 20 years ago, but put by pending the completion of the analyses; since then other samples of atmospheric dust have come into my possession and the results of their examination are now given.

Meteoric Dust from the Barrier Range, near Broken Hill. Collected by Mr. C. W. Lloyd, in 1896. Of a reddish colour, rather coarser in grain than the dusts from Menindie, Moruya, &c. The average size of the particles is 0·07 m.m., or 3/1000ths inch. It appears to be made up principally of water-worn quartz grains, stained with iron oxide, with some charcoal or carbonaceous fragments, also calcareous particles (concretions and fragments of shells), and a few black non-magnetic mineral fragments.

Analysis.

Moisture at 100°	2·30
Silica	79·10
Iron sesquioxide	2·97
Alumina..	10·58
Lime	2·00
Magnesia	traces
Loss on ignition	3·00
	99·95

Meteoric Dust, Pambula.—This sample was collected by Mr. H. Forde, on October 5th, 1899, who states that it fell all over the township of Pambula (land district of Eden), and bore the appearance of a thick red fog. This dust is an extremely fine and impalpable powder of a pale brownish tint. The average size of the particles is less than 0·01 m.m. As it apparently does not differ materially from the others, it has not been analysed.

Meteoric Dust from Menindie.—This specimen was forwarded to me by Mr. H. C. Russell, the Government Astronomer, on November 23rd, 1899, who stated that it had been collected by a friend during a recent red dust rain storm, who took great care to get it pure; on drying (under cover to keep the ordinary dust out of it) it split up into pieces and curled up like a dried clay. Of a reddish colour; under the microscope it appears to be composed principally of rounded quartz grains, some of which are reddish from a film of iron oxide. The average size of the particles is 0·25 m.m., or 1/100th inch. Mixed with the dust are some small pieces of calcium carbonate (concretions and fragments of shells) also some fragments of soft black readily combustible carbonaceous material, which may be water-logged charcoal, from bush fires or decayed wood; there are also a few particles of black mineral matter, probably chromite, but not yet examined.

Analysis.

Moisture at 100°	0·85	
Loss on ignition	2·20	
Silica	89·15	
Iron	1·06	
Alumina	6·39	
Lime	0·80	= 1·43 $CaCO_3$
Magnesia	traces	
Alkalis	traces	
	100·45	

The following from Victoria is added for comparison :—

"*Red Rain*" *Dust.*—Some of this dust was collected at Moonee Ponds, near Melbourne, from a shower which fell on December 27, 1896, over Melbourne and a considerable area in Victoria, and was examined by Mr. T. Steel, F.C.S. ("Report Aust. Assoc. for Advt. Science," Sydney, 1898). He regarded it as a sample of ordinary surface soil, derived from the weathering of volcanic rocks; it contained diatoms, &c., such as are usually found in fresh water deposits.

Dried at 110°. Moisture in air-dried sample = 6·09

Loss on ignition	10·70
Sand, insoluble and undetermined	66·23
Alumina	15·16
Soluble silica	0·75
Ferric oxide	4·68
Ferrous oxide	0·50
Lime	1·36
Sulphur trioxide	0·62
	100·00

For the sake of comparison the following analyses of dusts of undoubted volcanic origin are added; it will be seen at once that the atmospheric or so-called meteoric dust is very different in composition. Under the microscope the differences are still more strongly marked.

Krakatoa Ashes, collected at Batavia. Analysed by A. Sauer (*Jahrb. f. Min.*, 1884).

SiO_2	63·30
TiO_2	1·08
Al_2O_3	14·52
Fe_2O_3, FeO	5·82
CaO	4·00
MgO	1·66
MnO	0·23
Na_2O	5·14
K_2O	1·43
Loss on ignition	2·17
	99·35

Volcanic Dust, Barbados (*Geol. Soc.*, May 25, 1902; *Nature*, June 5, 1902). From the recent eruption, the ash consists principally of a plagioclase felspar allied to labradorite, hypersthene, monoclinic augite, and magnetite. The following analysis was made by Dr. Pollard :—

SiO_2	52·81
TiO_2	0·95
Al_2O_3	18·79
Fe_2O_3	3·28
FeO	4·58
MnO	0·28
(CoNi)O	0·07
CaO	9·58
MgO	5·19
K_2O	0·60
Na_2O	3·23
P_2O_5	0·15
SO_3	0·33
Cl	0·14
H_2O (105°)	0·20
H_2O (above 105)	0·17
	100·35

Volcanic Dust from Mont Pelée, Martinique, collected rom the deck of the S.S. *Roddam*, the only ship which escaped from St. Pierre (CHEM. NEWS, lxxxv., p. 282). Dried at 105 .

Silica	53·40
Alumina	21·00
Iron sesquioxide	9·50
Lime	9·70
Magnesia	2·00
Na_2O	2·33
K_2O	0·85
SO_3	0·90
P_2O_5	0·25
	99·93

The following hitherto unpublished accounts of falls of meteoric dust and dust fogs in New South Wales are, except the first, selected from a large number kindly placed at my disposal by Mr. H. C. Russell, F.R.S., Government Astronomer; they are of interest as showing the conditions under which some of the dusts were deposited.

One of the earliest accounts of dust storms in Australia is given by Strelecki in his "New South Wales and Van Diemen's Land," published in 1845. He says :—

"In sailing from New Zealand to New South Wales in the *Justine*, I was prevented making the harbour of Port Jackson for two successive days by the violence of the hot wind. The distance from the shore, on the parallel of Sydney, was sixty miles, and the heat exceeded 90°. The lee sails and reefs of the *Justine* were covered with a quantity of impalpable dust, which was at first mistaken for ashes, but on examination proved to be sand, containing one-fourth of aluminous and three-fourths of siliceous and metallic matter. Those who shape their course to the East Indies, by way of Cape Verde Islands, may have seen the same effect produced by the north-east African hot wind."

The following account was addressed to Mr. Russell :—

"*Times* Office, Murrurundi, Oct. 21, 1876.

"So far as I have been able to ascertain, the dry fog was first seen in the vicinity of Tamworth, at about sunrise on the morning of the 12th instant. In the various weather notices of different journals published north or west of that town, no mention is made of the phenomenon, such as would be expected had its appearance been observed in the districts they represent. The *Tamworth News* refers to it as obscuring the horizon from north-east to south-west, and as being the result of the refraction of the solar rays on passing through the depressed exhalations from the moistened earth. In this neighbourhood the conditions under which the fog appeared were quite different, its direction being rather from north-west to south-east, and its existence altogether independent of "moistened earth," the preceding night having been too mild in temperature to produce a very copious fall of dew. With these exceptions the accounts coincide in the general representation of the event already furnished.

"Its appearance and disappearance were alike sudden, considering the immense extent of country it appears to have covered, and its rate of progress was exceedingly rapid. At half-past five a.m. on Thursday, the valley of the Page was as clear as usual on fine mornings, but on the ranges a peculiar dense mist, in colour precisely like a dust-cloud, was seen advancing quickly towards the town of Murrurundi. At 6 o'clock the whole of the valley with the town and the surrounding mountains were enveloped in the murky haze, the atmosphere became oppressive as though a heavy thunderstorm were at hand, and the sun was so obscured that it could be viewed without the slightest inconvenience by the naked eye. No disagreeable odour accompanied the fog, but it caused a sensation similar to that experienced during the first downpour of rain upon a dusty surface, that oppressiveness to the senses generally that a continued fall of rain would be likely to relieve. In fact, had it not been for the strangely impalpable nature of the fog, it would have been considered as an extraordinary diffusion of dust in the atmosphere, consequent upon strong winds. No inconvenience

was occasioned to the eyes, the only discomfort being the comparative sultryness of the morning and the sense of oppression experienced. No dust was left by the fog, nor the slightest moisture; it remained for many hours a perfectly dry, dense, dusty looking mist enwrapping every object in obscurity for many miles around. Shortly after half-past eight a.m. it left the Page valley, and proceeded towards the south, driven before the wind which rushed along the passage between the mountains with great force. The general direction of the wind was nearly direct from west to east, but as usual in the valley its course locally was determined by the position of the mountains, and the fog in the lowest lands was driven off to the south at the time already mentioned, while a portion of it lingered about the hills until nearly midday; at the head of the Page, I believe, it was discernible in the afternoon.

"At Scone, twenty-five miles south of Murrurundi, the fog made its appearance shortly before 8 a.m., while Murrurundi was still enveloped in its mist. A gentleman resident in this colony for upwards of thirty years, and a very shrewd observer of the weather, happened to travel from Murrurundi to Scone during the continuance of the fog, and he states that he was surrounded by it the whole way. He started on the journey about an hour after the fog made its appearance here, and his impression was that the mist was travelling at a rate of more than fifteen miles an hour. After leaving the valley of the Page, the wind was found to be blowing stiffly from the west, but the fog remained at Scone until nearly midday, when it gradually cleared off.

"The manner of its disappearance from Murrurundi was somewhat sudden, and would give the impression that it was carried by the wind over the country at a considerable speed. But the fact of it having remained amongst the mountains so much longer, leads me to think that it was driven out of the valley as from a narrow passage by the increased force of the wind when compressed within the limits of the pass. The occurrence of winds in this part of different directions and force from those in more open country is too common to need further mention, and it is tolerably certain that in the open country the fog was not so visibly and directly influenced by the wind as it appeared to be at Murrurundi. It should be mentioned that the wind was not noticed until some time after the fog made its appearance; the air was at first still, heavy, and oppressive, but afterwards the wind rose quickly, with frequent gusts, which swept great quantities of dust along the main road, giving colour to the supposition of some persons that a similar wind had blown during the earlier part of the morning, raising clouds of dust, the finer portions of which were still being carried by upper currents of wind across the country. But this is only one of many explanations invented for the occasion, and without any knowledge of the extent of the fog; allusion to some others more distant from reason and experience is made in one or other of the extracts enclosed.

"At Singleton the fog appears to have been witnessed at seven o'clock, about half an hour later than at Murrurundi, while at Scone, nearly half-way between, it would appear to have not been observed until a later hour than either—between half-past seven and eight o'clock. If I remember rightly, its appearance at the Paterson was still later, and no record of its having been observed further south or east is procurable here. The Maitland and Newcastle papers make no editorial comment upon it, nor with regard to Newcastle journals has any reference whatever to the occurrence been made. I may add here that, as already stated, the Gunnedah, Armidale, Glen Innes, Tenterfield, and other papers published in the north and west, seem to have taken no notice of the phenomenon, so that thus far observation is limited to the districts between Tamworth and the Paterson.

"In answer to your question, 'Did it leave any dust; if so, was any collected?' I may repeat that no dust was observed to fall from the dark mist, but the occurrence of high winds raising the usual clouds of dust from the roads would hinder the attempt to distinguish between the dust deposited from either source unless the difference were very clearly marked. I am alluding now, of course, to observations made at positions within the reach of dust driven from the roads by high winds. In remoter places, I am informed, the only peculiarity remarked in the fog was its singular dryness, together with its discolouration, as compared with usual mists.

"From the best enquiries I have been able so make, such a fog has never been witnessed before by residents in the districts visited, and the subject has been very generally canvassed in the circles of the 'oldest inhabitants.' A general impression that it was the precursor of blight or an insect visitation existed, probably owing to the fact that some persons of years and education adopted this view of the occurrence and injudiciously (I think) gave their ideas to the less informed and more impressible of the residents. All were agreed, however, that the phenomenon had never been witnessed here before, whatever might be the opinions entertained respecting its origin or consequences.

"The time at which the fog first made its appearance in the different districts mentioned, seems to involve the subject in more difficulty than it presented at first to myself, but by correspondence I shall endeavour to obtain further and more precise information upon this point. After perusing your interesting paper and Humboldt's remarks upon dry fogs, with the more remote phenomena recorded by the Roman poet, I can find no parallel to this occurrence excepting in the appearance of cosmical meteoric dust, hypothetically alluded to in your concluding remarks."—H. Jones.

"*Times* Office, Murrurundi, Nov. 7, 1876.

"From enquiries made since my last, I have gleaned a few particulars, which, though imperfect, may be worth communicating. The most important of these have been supplied by Mr. George Armstrong, a gentleman of very extensive colonial experience, at present residing at Walcha. He informs me that the dry fog of the 12th ultimo was noticed near Bendemeer on the morning of that day, about six o'clock. He was out with some assistants looking after stock in the vicinity of Bendemeer, between that town and Surveyor's Creek, when his attention was attracted by an apparently heavy, wide-spreading cloud of smoke rolling over the distant mountains. He directed the notice of those who accompanied him to the strange appearance, and the impression left upon their minds was that an immense bush fire had occurred on the hills, causing the smoke they imagined to be covering the mountains. They rode in the direction of the mist, and soon discovered that its origin and nature were widely different from those already mentioned. In short, they found it to be a dry fog, of such an extent and density, however, as to render it quite singular. Mr. Armstrong is a native of South Australia, of which colony his father and uncle were amongst the earliest pioneers, and he has therefore the benefit of at least forty years' clear knowledge of the seasons and phenomena witnessed in these colonies. According to his account, these dry fogs, though not common, have occurred several times within his recollection, but have never had nearly so wide a range as that of last month. Many years ago he encountered one of these fogs at the head of the Wilson River, in the meridian of Capricorn; he was then engaged in driving stock, I think, and when approaching the Valley of Lagoons, witnessed a phenomenon similar to those under notice, but of a comparatively local character. More recently, while travelling with a large flock of sheep, he noticed a dry fog at Goonoo Goonoo, a station of the Peel River Company, near Tamworth, but this also was of limited extent. The most notable of these occurrences, he says, occurred in South Australia in 1836, in the month of April. That colony had only just been formed at that time, and the phenomenon excited a good deal of apprehension in the minds of the settlers. There can scarcely be any evidence I imagine, of the extent over which the fog of 1836 was observed, as the colony had not then been opened up. The aboriginals

associated the occurrence with some mischievous event, the nature of which they could not define. I omitted to mention that at Bendemeer there was no wind perceptible immediately before the fog appeared, but shortly afterwards a slight westerly wind sprang up. The direction in which the fog appeared to the view from Bendemeer was about south-west by west. The fog appeared to annoy the horses the party were riding. The fog covered the Swamp Oak Creek, Surveyor's Creek, and intermediate country.

"This is the extent of my information respecting the fog as it appeared at Bendemeer, but Mr. Armstrong has promised to furnish me with memoranda of this and other dry fogs which he has preserved. If I should receive them I need not add that they will be speedily forwarded to you.

"A friend who visited Clarence Town a day or two after the 12th ultimo, tells me that the fog was the topic of general remark during his stay. In that locality it is said to have presented a dull grey leaden hue, but otherwise preserved the peculiarities noticed elsewhere.

"At Bellevue, near Scone, a number of aboriginals are located, and the fog has not passed them without observation. They take it to be a sign of approaching drought, and they tell of similar appearances having been noticed in past years. This at present is all the additional information I have to offer. I am expecting more in answer to letters sent to different persons likely to have observed the phenomenon."—H. Jones.

"P.S.—I have not been able to secure any dust, or learn of any having been deposited by the fog or whatever the phenomenon should be termed."

"Yabtree, Gundagai, Dec. 23, 1880.

"Having seen your paragraph in *Herald re* dust storm that occurred on Wednesday, 15th instant, will state herein the storm as observed here. Yabtree is on the Murrumbidgee, about equal distance from Gundagai and Wagga. About 1 p.m. on the 15th the sky became overcast, sun obscured, and some hills about two miles away partially so; they had the appearance of heavy rain falling; wind strong from about W.N.W.; in a few minutes the dust made its appearance, it was very fine. At first I thought it was smoke coming from bush fires, and although the house was closed, in a few minutes everything inside was covered with fine dust. The storm lasted until about 6 p.m., the sun having been invisible the whole time and wind in nearly same direction; then a few drops of rain fell, the wind fell away to almost a calm, and sky partially cleared, only few rain clouds passing slowly to east; a few more drops of rain fell about 8 p.m., after which the night was a clear one. There are no roads near Yabtree from which the dust could come, so I came to the conclusion that it was due to a storm, and felt disappointed by not seeing any remarks thereon in telegrams in Thursday's *Herald*, except from one station, Euabalong on the Lachan River, about 200 miles W.N.W. from here; the direction from here to where the *Potosi* passed the mud shower, is about E.S.E., so the Euabalong, Yabtree, and *Potosi* storms were most likely likely one."—R. F. Horsley.

"Tumut, N.S.W., Dec. 23, 1880.

"I see by your letter in the *Sydney Herald*, dated Dec. 20, that you are anxious to collect all the information you can get as to the showers of mud that fell on board the S.S. *Potosi*, and also at Moruya, on Wednesday, the 15th December. At Tumut the morning opened calm and hot; about 10 a.m. the wind began to rise and whirled the dust along in thick choking clouds, which gradually mounted higher and higher into mid-air until all the surrounding hills were blotted out, or only seen occasionally, as though a heavy thunderstorm was raging in their vicinity. Thermometer standing, 12.30 p.m., at 94° in the shade, in about the coolest spot to be found in Tumut, viz., large open shed at the Brewery, with a thick bark roof, where the beer is cooled before going into the casks; on this occasion the cooling table was covered with cold water to keep the seams tight while no brewing was going on.

"As Wynyard Street was the main channel of this terrific storm of dust, at times one side of the street was quite invisible to the other, shops had to close all doors, and even then a very fine deposit of dust remained on everything after the storm was over, which eased itself down as the sun declined, and was entirely over at sunset. The fine dust seemed to have attained an altitude of from one mile to a mile and a half, and was travelling from about W.N.W. to E.S.E. (no compass here). When over, the roads were swept clean of fine dust, and the coarse sand lay in regular ridges, the same as waves leave it on the sea beach. Perhaps Adelong could give further information, as the storm came from their direction. No doubt the fine dust travelled out to sea until beat down by the rain, for I see by the public prints that you had this storm at Sydney the same night. I enclose some of the fine dust obtained from nooks and corners of elevated places, so that you may compare it with that your Moruya correspondent sent you."—Edward Alleyne.

"Moruya Heads, Meteorological Station, 22nd Dec., 1880.

"I have forwarded three samples of the mud or dust shower of the 15th instant; the samples have been carefully collected with a very fine brush, and I think contain very little of any other matter than that which fell during the shower; a great deal has been blown away since the 15th, though now all the bushes, leaves, small trees, &c., show it very plainly. On the morning after the shower a few pounds weight could have been collected from tubs, buckets, rain guage, &c., but it was all thrown away.

"Concerning the shower, no particular notice was taken of it, the drops were large. It had been gloomy all day and threatening, and a low barometer; we had a southerly squall about 6 a.m., which cleared off about 8 o'clock, mizzling rain at 9 and cloudy, wind light southerly, with a smart shower at 10, then light showers until 2 or 3 o'clock the following morning. At 5 a.m., 16th, the weather was fine and clear. We had a quantity of clothes on the grass all night, which were all covered with mud, yet only thought it strange how it came there, until reading about the *Potosi* steamer having been in such a shower. She must have been about 40 miles south of the Moruya heads at the time. I have not heard of it being at any other place than Moruya, and a few miles along the south coast; it looks very much like the rust on wheat."—R. M. Tranent.

"Yaas, 23rd December, 1880.

"I noticed by Tuesday's *Herald* that you wish to get information about the late dust storm. I am informed by several parties that the storm rose a long way back, most of the dust rising off the stations between the Lachlan and Darling, crossing over Condobolin, Euabalong, and Forbes, about 12 o'clock on Wednesday morning, the 15th. I have been living in the Cobar district many years, and always found the dust very bad in summer, especially in very dry times. A flock of sheep going in to get water at a tank will rise the dust so that it can be seen plainly at a distance of 30 and 40 miles, travelling in the air the same as smoke from a bush fire (and it takes an experienced hand to tell the difference). I may mention the dust passed over Gunning between 5 and 6 o'clock on Wednesday evening, 15th, the wind being from south-west."—C. E. Armitage.

"Wingen, Jan. 23rd, 1884.

"We have had here a rather remarkable appearance in the air. On Sunday morning, January 20th, the thermometer record for the previous 24 hours was 88 max., 53 min., with wind blowing from the west, and that night we had a light thunderstorm, with 41 points of rain. On Monday, the 21st, the thermometer record for previous 24 hours was 98 max., 60 min., and the wind blowing strong from the north-west, and the country was covered all day with a light haze which did not appear at all like smoke nor like ordinary dust. This continued all day, and on Tuesday morning the thermometer record for the previous 24 hours being 84 max., 55 min., the wind blowing strong

all day from the same point, the country was still covered with haze. To-day, Wednesday, the 23rd, the thermometer record for previous 24 hours was 81 max., 57 min., wind blowing from the same point, the haze has quite disappeared. The wind during the whole time seemed cool and moist, which seemed the more remarkable as we have for weeks past been having hot dry winds from the same point. The idea which suggested itself to me was that there had been heavy rain in the north-west, as the feeling in the air and the appearance was much like what sometimes occurs in Sydney when a southerly buster comes up after a very hot day."—W. E. Abbott.

"*Dust Storm* of August 14th, 1885, as seen at Hay.—The night of the 13th August, during the ride in the coach from Gunbar to Hay, was most beautifully clear. At the commencement of the last stage, 20 miles from Hay, at 5 o'clock a.m., August 14th, the wind was blowing pretty freshly from the north. Later on there was a magnificent sunrise, the air being as clear as could be. On reaching Hay about 7.30 a.m., the wind was blowing strongly and increased up to 10 a.m., when it was blowing in heavy gusts from the north. It continued in this way till about 2.30 p.m., when it gradually grew calmer and veered to the south-west. At 7.30 a.m. the barometer stood at 29·396. It fell steadily until 2 p.m., when it commenced to rise. About 10 a.m. the whole place was enveloped in a light reddish-brown fog, which continued all day. The particles of dust composing this fog, if it may be so called, being too fine to be seen, no motion was observed, although the wind was blowing in strong gusts. The day was warm and rather close, the temperature being 70°. A light reddish-brown dust was deposited on everything. The wind got much calmer towards evening, and after sunset a slight shower of rain fell. The morning of the 15th was fine and rather cold. There were a few cirrus clouds, the white back-ground of which showed a slight reddish tinge in the air, which could not be seen against the blue sky. The rain guage showed about 0·003 rain with a deposit of mud about 0·001."—J. Arthur Pollock.

"Buckingbong, Narandera, 13th Feb., 1885.

"Narandera and the neighbourhood seem to be about the worst places visited. As far as I can learn, the storm travelled from Hay to Narandera in 1¼ hours, and from Narandera to Wagga 1 hour, but the wind on the surface did not I think exceed 20 to 30 miles an hour, nor was there much dust near the ground. The wind in the clouds seemed of a whirl-wind nature, the appearance before darkness came on being very wonderful, the clouds were rolling and rolling over and under one another. You will probably know that the storm struck Narandera about 2.15 p.m., and total darkness lasted for 15 minutes, succeeded a like time by a sky of red so brilliant you could scarce look at it. I may mention the darkness was blacker or more intense by far than the darkest night. I have interviewed many people since, men who have been in the colonies 50 years or more, but they aver they never saw anything like the storm of Friday, February 6th."—B. Blair.

"Kymba, August 15th, 1885.

"At 9 a.m. the wind was N.E. moderate, with the sky slightly hazy, and a mild feeling in the air, similar to what would be experienced on a mild summer morning, although the minimum temperature during the night had been 30°. The barometer (an aneroid) registered 28·50, being 0·10 lower than at 9 p.m. the previous night. By noon the haze had gradually thickened, and the wind had veered to N.W., but came in variable gusts, and the barometer had fallen to 28·35. Shortly after noon, the clouds which came in the wake of the wind, which had increased to a gale, assumed a peculiar aspect—a dun or salmon colour, and the surrounding hills became enveloped in a light yellow, foggy haze, which was thought to be rain. At 3 p.m. the barometer registered 28·33, and remained steady till 6 p.m. The gale blew with considerable violence during this time. After sunset rain commenced to fall in showers, with strong gusts of wind, and with the rain a quantity of mud fell, which bespattered everything. As an instance, iron tubs placed under spouts had one-eighth of an inch of a red deposit at the bottom this morning, and roofs and out-buildings bore traces of the discolouration. Twenty-seven points fell up to 9 o'clock this morning, and the barometer has been gradually rising since, although light showers have fallen at intervals through the day. As a mud or dust storm seems so unseasonable at this time of the year, I have dried a small quantity of it, and enclose in this letter, as it may be useful in your observations on the subject. The country in this immediate neighbourhood is too damp from the effect of the recent showers to furnish any dust. I may state that the altitude of this place above sea level is 1036 feet, according to Mr. Railway Surveyor Jamieson, who kindly informed me some time ago. The highest reading of the aneroid has been 29·36 since I have had it."—R. J. Barr.

"Narandera *Argus* Office, August 24th, 1885.

"Some time since Mr. Bryce Blair, of Buckinbong Station, near Narandera, requested me to forward to you details of the very severe dust storm which passed over this district on Friday, the 6th of February last. I enclose herewith extracts from the *Argus* of the 7th of February, which of course can only be accepted from a paragraph point of view. My personal experience I give you briefly in narrative form :—' I returned to my office shortly after two o'clock ; there was at that time every indication of a heavy dust storm coming from the west ; in the course of half an hour the town was enveloped in dense clouds of red sand, that was no more than the usual experience at intervals during the summer, but suddenly there came a black column (like the densest smoke in appearance) which made the place darker than the darkest night I ever experienced ; it was, in fact, the first occasion upon which I realised absolute darkness. Many people in speaking of it afterwards assured me that they had, from very fear, to remain where they were when overtaken by this cloud ; for myself, I may say that in my office just before the storm, I had moved from the window, and suddenly I was so confused by the intense blackness that I could not possibly tell where the window was placed, and though knowing perfectly well in what part of the room lucifers, &c., were usually kept, I had to grope about for some time before I could secure the means of kindling a light. As a matter of fact, I can say nothing stronger than that it was darkness that could be felt."—Geo. Eldridge.

"Gundaroo, 30th December, 1885.

"Such an unusual and strange occurrence took place here this morning that I thought I would communicate it to you. About half-past six a.m.. on looking out the whole of the hills in the distance, west and south, seemed enveloped in a cloud of dust or fog which gradually rose and worked round south to east. About seven, the hills west were cleared, but the dust hung in mid air like a cloud, excepting at two or three places, where it hung as if the dust was falling like a shower of rain ; at about a quarter past seven it had all blown in a body to the south, which was so dense that the hills only a short distance away could not be seen, and then it came blowing down direct north ; it then took a north-west direction and died away. Now at a quarter to eight a.m. there is hardly a breath of air, with the sun shining out hot ; during my thirty-one years' residence in this part I never saw the like before, and thought such a strange occurrence deserved notice being taken of, and this is my reason for troubling you with the details."—William Affleck.

(To be continued).

New Publication.—The first number of the *Journal de Chimie Physique* will appear shortly. It will be published in Geneva by M. Philippe A. Guye, Professor of Chemistry at the University of Geneva, and will deal with all matters concerning electro-chemistry, thermo-chemistry, radio-chemistry, mechanical chemistry, and stoichiometry, and will contain abstracts of all papers on physical chemistry appearing in other countries, &c.

NOTICES OF BOOKS.

Il Moto dei Ioni nelle Scariche Elettriche. ("The Movement of the Ions in the Electric Discharge"). By Augusto Righi. Bologna: Nicola Zanichelli. 1903.

This reproduction of a lecture given in March before the Italian Electro-technical Society has been slightly enlarged for publication. Though the author apologises for any defects or deficiencies which might naturally be expected to characterise a lecture delivered under the circumstances spoken of in the preface, it is difficult to see in what respects any improvement could be made in the treatment for the benefit of the general reader, previously unacquainted with this most interesting and important subject, branches of which Prof. Righi is at the present time investigating with the originality and thoroughness which mark his work. The lecture aims at being chiefly historical and descriptive, and speaks more of what conclusions have been actually arrived at than of what is as yet unexplained; thus, while containing nothing new, it is an eminently readable account of recent work, and all interested in the subject will find it a useful introductory sketch. Some debatable statements must necessarily be expressed more or less positively in a sketch of this kind, but it is in all respects very fair and well-balanced.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 25, June 22, 1903.

Preparation of Carbides and Acetylenic Acetylides by the Action of Acetylene Gas on the Hydrides of the Alkalis and Alkaline Earths.—Henri Moissan.—The author finds that at a temperature of 100° the alkaline and alkaline earth hydrides react on acetylene gas, producing acetylenic acetylides, and setting free hydrogen. This reaction is important because it allows of the transition easily, and at a low temperature, of hydrides into carbides. It is enough to heat acetylenic acetylide in a vacuum for dissociation to take place, and the acetylene group to be destroyed and the corresponding carbide produced. This process, therefore, constitutes a new method of preparation of the carbides of the alkalis and alkaline earths. At this temperature of 100°, ethylene and methane do not react on the different alkaline hydrides.

Influence of Solvents on the Rotatory Power of Certain Molecules. Derivatives of Camphor.—A. Haller and J. Minguin.—Benzene always exercises an action on the rotatory power of certain camphor compounds, but the differences are not so marked as in the case of molecules possessing the complex $\begin{matrix} C{-}\overline{R} \\ | \\ CO \end{matrix}$.

Estimation of Vanadium in Alloys.—Paul Nicolardot.—The methods actually known for the estimation of vanadium are either very long or not very accurate. The author modifies Sefström's method for the detection of vanadium in iron, to render it capable of a quantitative application. Steels and irons, containing vanadium, when attacked by sulphuric or hydrochloric acid, leave a black residue consisting chiefly of graphite, silica, and a little vanadium. If all chance of oxidation is removed, the vanadium remains behind in the metallic state, no trace of this metal being found either in the dissolving liquid nor in the gaseous products evolved. A perfectly accurate and fairly rapid means of estimating vanadium in alloys may thus be employed.

Etherification of the Hydracids.—A. Villiers.—The etherification of the hydracids presents a certain number of anomalies which can be attributed to two different causes: —(1) The existence of hydrates formed by the hydracids, which can be distinguished from those of sulphuric acid by the dissociation which takes place under the influence of heat; (2) the production of ordinary ether with liberation of water. This production is more abundant the higher the temperature, the contrary taking place with sulphuric acid, in which case the temperature influences the rapidity of the formation of ether and not the final proportion.

Benzoyl-derivatives of Hydrazobenzene.—P. Freundler.—The author prepares monobenzoylhydrazobenzene, $C_6H_5{-}N{-}N{<}^{CO.C_6H_5}_{C_6H_5}$, by effecting the benzoylation in pyridic solution of hydrazobenzene. He also examines the properties of this substance.

Certain Compounds of Gold Chloride and Pyridine.—Maurice François.—Chloroaurate of pyridine, $C_5H_5NHCl.AuCl_3$, is only stable in presence of hydrochloric acid and gold chloride. Under the action of hot water it easily yields a compound, $C_5H_5N.AuCl_3$. There also exists a compound, $(C_5H_5N)_2AuCl_3$, which can be prepared either anhydrous or hydrated. The constant production of the compound $C_5H_5N.AuCl_3$, as distinguished from the other compounds of pyridine and gold chloride, by the action of water or heat is remarkable.

Phenylic Substitution in Phenylmethanes; their Carbinols and their Chlorides.—Jules Schmidlin.—The author measures the heat evolved or absorbed during the phenomena of substitution, and in particular during the substitution of hydrocarbons amongst themselves, and with hydrogen. The heat of substitution is measured by an indirect method, by which the number is deduced from the difference between the heat of formation of the compounds from their elements, these being themselves calculated from the heats of combustion.

Preparation of Nitrous and Nitric Ethers.—L. Bouveault and A. Wahl.—Nitric ethers can be prepared by the action of nitric acid on alcohols, and concentration in the cold either over sulphuric acid or under reduced pressure. In either case each particular alcohol must have its own conditions of concentration and temperature. Nitrous ethers can be prepared by the action of the vapour of nitrous acid on alcohols.

Chlorine Derivatives of Methylene Chloroacetate and Diacetate.—Marcel Descudé.—Acid chlorides easily combine with polymerised formic aldehyde when in the presence of zinc chloride. During the reaction two groups are formed, $\begin{matrix} R{-}COO \\ Cl \end{matrix}{>}CH_2$ and $\begin{matrix} R{-}COO \\ R{-}COO \end{matrix}{>}CH_2$. Methylene chloroacetate or monochlorated methyl acetate can be obtained by the direct action of chlorine on methyl acetate. The action of chlorine can be pushed further, chlorated and less well known bodies being obtained, but the substituting action of the chlorine takes place on the CH_3 group directly attached to the oxygen.

Bodies of the Pyranic Series.—R. Fosse and A. Robyn.—In a previous paper one of the authors examined the oxidising power of certain pyryl salts. These exercise a remarkable action on alcohol, oxidising it into aldehyde, and being transformed themselves into pyranes. The authors now further investigate this reaction, not only to establish a generality, but also to obtain new pyranes, of which only a small number have been at present prepared.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xxix., No. 2.

Bipolar Electrodes with an Insoluble Anode.—André Brochet and C. L. Barillet.—The authors have found that in electrolysis with insoluble bipolar electrodes, the flow of the current is affected strongly on account of phenomena of polarisation. The quantity of electricity

traversing the metallic strip is extremely small, while that derived from the liquid is relatively considerable.

Bipolar Electrodes with a Soluble Anode.—André Brochet and C. L. Barillet.—Already noticed.

Remarks on the Use of Bipolar Electrodes.—André Brochet and C. L. Barillet.—As a result of their researches on bipolar electrodes, either with soluble or insoluble anodes, the authors have come to the conclusion that soluble anodes influence the flow of the current in the same manner as insoluble ones. To get the best effects with bipolar electrodes, they should form water-tight compartments; the spaces reserved for circulation should be as narrow as possible to prevent losses by derivation. In an electrolyser metallic pieces may be employed, not communicating with the electrodes, not only if the metal acts as an insoluble anode, but more particularly if it acts as a soluble anode.

Complex Salts of Platinum. Plato-oxalonitrites and Plato-oxalonitrous Acid.—M. Vèzes.—Already inserted in full.

The Polymers of Methanal.—Marcel Descudé.—The commercial product known as trioxymethylene does not answer to the formula $(CH_2O)_3$. The various commercial polyoxymethylenes do not all behave in the same manner with certain compounds, especially with chloride of acetyl. With some, in the presence of chloride of zinc, there is instantaneous and integral union, molecule for molecule, in the cold; with others, under the same conditions, there is a commencement of the reaction, but the greater portion of the polyoxymethylene remains unattacked. The author has made a comparative examination of these different products. He found that their solubility in water is the more easy in proportion as their reactional activity is the more energetic. He thought that this might be due to a different state of physical aggregation, the molecules being less apt to take part in a reaction, or go into solution, as their state of condensation is more advanced. The results obtained by experiment confirmed this opinion. He found, in fact, that the product is more active, more easily soluble in water, and its proportion of carbon is further from 40 per cent as it becomes more volatile. Further, that the small quantity of water it may contain does not seem to play any active part, since it can be completely eliminated in some cases without the properties of the bodies being modified in any manner.

The Variations of the Densities of Hydro-alcoholic Mixtures.—H. Vittenet.—As the densities of mixtures of water and alcohol had not been determined for solutions containing less than 10 grms. of ethylic alcohol per litre, the author has undertaken to fill up this gap. The results obtained are given in the following table, and are sufficiently clear not to require any further comment:—

Proportion of the hydro-alcoholic mixtures.		Weight in grms. of equal volumes of the hydro-alcoholic mixtures.	Densities.
Water.	Alcohol.		
100	0	109·8504	1·
999	0·9977	109·8294	0·99980
998	1·9469	109·8082	0·99961
997	2·9922	109·7860	0·99941
995	4·9865	109·7460	0·99904
993	6·9809	109·7024	0·99865
990	9·9726	109·6388	0·99807

Acetal and its Products of Hydrogenation.—André Kling.—Already noticed.

No. 3.

The Temperature of Inflammation and the Combustion in Oxygen of Three Varieties of Carbon.—Henri Moissan.—Already noticed.

Hydrogen in the Air; its Influence on the Determination of the other Gases, and the Density of Nitrogen.—Armand Gautier.—This paper is to a great extent a criticism of the opinions expressed by M. Leduc and Lord Rayleigh on the proportion of hydrogen stated by the author to be present in the air.

Application of the Theory of Electric Batteries to the Quantitative Separation of Metals.—A. Hollard.—Already inserted in full.

Action of Isocyanate of Phenyl on some Free Oxyacids (IV.).—E. Lambling.—In previous papers the author has described the products of the action of isocyanate of phenyl on the ethers of a certain number of oxyacids. He further examined the action of the carbanile on the same oxyacids in the free state. He now goes on with the examination of the phenylurethane of the anilide obtained with some of the oxyacids used in the course of his research. The experiments described are the action of isocyanate of phenyl on glycolic acid, on lactic acid, on trichlorolactic acid, on *a*-oxybutyric acid, on *a*-oxyisobutyric acid, on phenylglycolic acid, and on benzylic acid.

The presence of Volemite in some Primulaceæ.—J. Bougault and G. Allard.—Already noticed.

Derivatives of Cyclohexene by Addition.—Leon Brunel.—Already noticed.

The Chloride and the *d*-Camphosulphonate of Benzylquinolinium.—A. Reychler.—The observations made in this research seem to show that the direct synthesis of chloride of benzylquinolinium produces the substance $Cl—\begin{matrix}R'\\ <\\ R''\end{matrix}\!\!\!

MISCELLANEOUS.

Institute of Chemistry of Great Britain and Ireland.—*Examination in Biological Chemistry.*—The Council have resolved that the Examination in Biological Chemistry, hitherto a Branch of the Final Examination for the Associateship, shall in future be open to Fellows and Associates of the Institute who desire to obtain testimony of their knowledge in this branch of work. The Examination, while suited to those intending to practise their profession in its relation to the chemistry and bacteriology of water, sewage, and effluents, can also be taken by those who are interested in the chemistry of Brewing, and other industries involving both chemical and bacteriological knowledge, and by pathological chemists.

The Final Examination for the Associateship in the Branch of Biological Chemistry.—An Examination in the Branch of Biological Chemistry will be held at the Laboratories of the Institute, 30, Bloomsbury Square, London, W.C., on Tuesday, October 20, 1903, and three following days. The Examination is open to any Candidate whose application for admission to the Final Examination has been accepted by the Council, and to any Candidate who has passed the Intermediate Examination of the Institute. Candidates desirous of presenting themselves are required to notify the Registrar on or before Tuesday, September 15, 1903, when the list of Candidates for this Examination will be closed. The Examination will extend over four days, and may be theoretical, practical, written, and oral, and the syllabus will include the following:—Biological Chemistry, with special reference to the Chemistry and Bacteriology of Foods, Water, Sewage, and Effluents, and the practical applications of Biological Chemistry to Industries. Candidates presenting themselves in any Branch of the Final Examination are expected to possess a general knowledge of all branches of Chemistry in addition to a *thorough* knowledge of the particular Branch of Chemistry selected. The Examiners are at liberty to apply any test they think desirable, either *viva voce*, or by writing, or by experimental work, in order to obtain evidence as to the practical knowledge of Chemistry possessed by the Candidate. Candidates must be familiar with the use of such scientific instruments as are commonly found in chemical laboratories. Any Candidate for the Final Examination may present a thesis upon any chemical subject to which he has paid special attention; and the thesis, if approved by the Examiners, may be taken as part of the Examination. Candidates are also at liberty to submit note-books containing records of any work done by them which have not already been inspected by the Examiners. The contents of note-books will be taken into consideration.

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SEPARATION OF SOLIDS IN THE SURFACE-LAYERS OF SOLUTIONS AND "SUSPENSIONS."*

Observations on Surface-membranes, Bubbles, Emulsions, and Mechanical Coagulation.

(Preliminary Account).

By W. RAMSDEN, M.A., M.D., Oxon., Fellow of Pembroke College, Oxford.

In a paper published in Du Bois Reymond's *Archiv. für Anatomie und Physiologie*, in 1894 ("Physiologische Abtheilung," pp. 517—534), I showed that mere agitation of various proteid solutions brought about a separation of some of their contained proteid in the form of fibrous or membrano-fibrous solids, and that it was possible in this way to coagulate and remove the whole of the proteid from solutions of egg-albumin. It was proved also that these de-solutions and coagulations of proteid were not due to the action of enzymes, heat, or surface evaporation, and were not appreciably affected by the nature of the gas in contact with the liquid, or of the vessel in which the agitation was effected.

A prolonged series of further experiments, undertaken with a view of ascertaining the precise cause of this phenomenon, has led me to the discovery of an important, but hitherto unnoticed physical fact—namely, that, quite apart from evaporation, solid or highly viscous coatings are spontaneously, and more or less rapidly, formed on the free surfaces of all proteid solutions.

By purely mechanical means these free-surface coatings can be heaped up to form visible solid masses of proteid, which in some cases is not only "de-soluted," but at the same time coagulated and rendered permanently insoluble in the mother-liquid.

By extending the range of my experiments, I have been led to the further conclusion that similar coatings of solid or highly viscous matter occur on the free surfaces of a large number of non-proteid colloid solutions, of fine and coarse "suspensions," and of a few apparently crystalloid solutions, and that they are formed also at the interfaces of every pair of liquids which, without being of high viscosity, are capable of forming persistent emulsions.

The explanation of these spontaneous de-solutions of previously dissolved matter at the free surfaces must be sought in the observation, which I have found to hold good in all cases hitherto examined, that the matter which accumulates possesses the property of lowering the surface-tension, and, therefore, the "surface energy," of the free surface of water.

On dynamical grounds, the most stable arrangement of any solution, taking surface-tension considerations only into account, must be one accompanied by minimal "surface energy." A dissolved substance, if it increases the potential energy of a surface, will tend to leave that surface, or if it diminishes it, to accumulate at that surface. This principle has been recognised as holding good in crystalloid solutions (*vide* J. J. Thomson, "Application of Dynamics to Physics and Chemistry," p. 251), but has not hitherto been shown to apply to colloid solutions and coarse "suspensions."

The same considerations may be applied in explanation of the accumulations observed at the interfaces of liquids forming persistent emulsions.

The formation of surface pellicles, the separation of various solids by mechanical treatment adapted to produce heaping up of surface-films, the power of forming moderately persistent bubbles possessed by various limpid solutions, and the power of forming persistent emulsions possessed by various immiscible liquids, are all explained (in the numerous cases where there is no evidence of chemical change) as due to diminution of the surface-energy brought about by accumulation of certain dissolved or suspended matters at the surfaces concerned, and to the physical properties of the accumulated material.

It is remarkable that the very common occurrence of these free-surface accumulations has hitherto escaped general notice. Doubtless this is due to the extreme delicacy and fragility of the solid coating, and to its generally rapid re-solution, when by contraction of the surface it is heaped up in local excess, or when by the substitution of some other surface, the reason for such accumulation has been removed. For the production of *visible* masses of solid, or of deformed angular bubbles, it is in fact necessary that the surface-solid shall either be rendered insoluble by the mechanical treatment to which it is subjected, or shall be heaped up more rapidly than it is re-dissolved.

Full details of the methods employed, the control experiments made, and the results obtained, together with references to the work of others in the same field, I hope to publish shortly. Meanwhile, a brief summary of the main points will be found in the following observations:—

1. The presence of a free (*i.e.* gas) surface is essential for the production of the de-solutions and coagulations described in my previous paper.

2. By simple and gentle mechanical means adapted to produce heaping up of the surface-films, large masses of solid ("mechanical surface aggregates") can be separated out from all proteid solutions, and from a large number of colloid solutions and suspensions (*vide* table at end of paper). In the three cases where the dilution-limit has been ascertained, solid "mechanical surface aggregates" have been obtained from liquids containing as little as one part of dissolved or suspended solid in 1,000,000 parts of water.

3. The separated solids differ greatly from one another in the rapidity and completeness of their re-solubility in the mother liquid, and they are sometimes insoluble and "coagulated."

4. They may have a delicate membranous, membrano-fibrous, or fibrous structure, simulating that of various biological tissues, or they may consist of particles lying loosely side by side (*e.g.*, sulphur).

5. The film of the free surface of all proteid solutions, and many of the various solutions or suspensions which yield solid "mechanical surface aggregates," exhibits a specially high viscosity, not met with in the bulk of the solution. This "special superficial viscosity" develops at very different rates in different solutions, and attains very different degrees of maximal intensity. In some solutions (*e.g.*, egg-albumin, saponin) it develops with great rapidity; in others (*e.g.*, serum-albumin, methyl-orange, ferric acetate, mastic, &c.) several minutes, or even hours, may be necessary for any considerable development. Evaporation hastens its development, but is not essential. Slight convection currents have a powerful accelerating influence, but are essential only when the suspended solid is indiffusible. The nature of the gas in contact with the "solution" is a matter of indifference, provided it be chemically inactive.

6. In most cases the "special superficial viscosity" is accompanied by a special superficial resistance to "shear." This is often so intense that a magnetised needle floating on the solution is capable of rotating the vessel containing the solution, if this be floated on water or suspended by a fine thread, and the needle be exposed to the attraction of a magnet.

7. The presence on a liquid of a thin coating of matter (even of liquid) which diminishes the "surface energy"

* A Paper read before the Royal Society, June 18, 1903.

would account for some "special superficial viscosity" (Marangoni), but would not account for superficial resistance to "shear," unless the coating of matter were solid or highly viscous and also coherent.

8. Bubbles of solutions of egg-albumin, caseinogen, and saponin exhibit remarkable phenomena, which show that the bubble-film as a whole is very imperfectly elastic, and is covered with solid membranes. Egg-albumin bubbles are deformed on collapse by the formation of persistent folds of solid proteid in the bubble-film. Bubbles of pure saponin solution, containing 0·01 per cent or more of saponin, fall on collapse into innumerable shimmering folds containing isolated curved rods of *solid* saponin, although water is capable of dissolving at least 2500 times this amount.

The collapsing bubble assumes extraordinary shapes, with sharp angles (as observed by Plateau), and when a hanging bubble is broken, a *ragged* curtain of bubble-film, which instantly becomes dull and opalescent, hangs for some five or ten seconds from the edge of the supporting tube.

9. The presence of such solid membranes on a bubble must contribute greatly to its persistence. Further, the mere presence of solid particles on the surfaces of a bubble has, in many cases, been found to add greatly to its persistence, even when, judging by the absence of a special resistance to shear in the film of a free surface of the solution, such particles are not appreciably coherent, but lie loosely side by side (*e.g.*, in suspensions of sulphur, picric acid, quinine bisulphate, salicylic acid).

In the cases quoted, a bubble of air can be seen to pick up the particles in suspension as it passes through the liquid, and to retain them obstinately when it reaches the surface and comes to rest, so that the bubble becomes thickly coated with solid particles, although the liquid contained only a small quantity of suspended solid, and this solid is specifically heavier than the solution.

10. Every solution capable of forming moderately persistent bubbles, which has hitherto been examined, has yielded solid or highly viscous mechanical surface aggregates. This very remarkable fact indicates that the power of forming such bubbles is due to the presence of matter which has accumulated at the free surfaces in a solid or highly viscous condition. The cohesion of the matter, so as to form an appreciably coherent membrane, is apparently not essential, but it occurs in most cases where the bubble is very persistent.

Plateau recognised this association of the power of forming persistent bubbles with a special superficial viscosity and a diminished surface-tension, but did not connect these phenomena with the formation of a coating of matter derived from the solution, and specially concentrated at a free surface (*vide* "Statique des liquids," pp. 69—71).

On theoretical grounds, the presence of a thin film of liquid, even of low viscosity, on the free surfaces, should also be capable of increasing the persistence of a bubble if the liquid be such as diminishes the surface energy of the mother solution, but increased persistence brought about in this way appears to be very slight compared with that occurring when the coating consists of solid or highly viscous particles.

11. The effects which the presence of solid particles in the surface layer exercises upon the persistence, size, and other properties of bubbles, depend on many factors. Many solutions in which surface accumulation of solid undoubtedly takes place have been found incapable of forming large or persistent bubbles. The size of the particles, their surface tension relations, the rate of their accumulation, the rate of their resolution when forced by mechanical means into local excess, and the elasticities and flexibility of any membrane formed, are all concerned in conferring on different bubbles the marked individuality which characterises them, and in making the formation of large or persistent bubbles possible. Solid particles, which diminish the surface energy of the free surface, may be regarded as adding in three ways to the persistence of a bubble:—

i. By serving as *points d'appui* (*cf.* Frankenheim, "Die Lehre von der Cohäsion," Breslau, 1835).
ii. By actual contact, friction, or cohesion of the particles, opposing local disturbances of the film.
iii. By opposing such de-formation of the surface as tends to expose a new surface with higher surface-tension (*i.e.*, like oil on water, by the effect of the surface coating in diminishing the superficial energy).

12. It has been demonstrated that an actual solid membrane forms around the globules of several persistent emulsions, and at the contact interfaces of several pairs of liquids capable of forming persistent emulsions (*e.g.*, pure neutral olive oil and saponin solutions).

The membrane manifests itself by producing the following phenomena:—

i. Intense viscosity peculiar to the interface, absent at the interface of pure water and the other liquid, and developing only when an emulsifying substance is added to one or other of the liquids.
ii. Persistently deformed sharply angular and grotesque shapes of the emulsified globules.
iii. Folds of semi-opaque membrane when the surface of separation is subjected to appropriate de-formation.

Such direct optical evidence of the presence of a constraining membrane separating liquids which form persistent emulsions is exceptional or, if it occur, is usually fugitive (*cf.* air-bubbles). An intense "special interface viscosity," pointing to the presence of solid or highly viscous matter, has, however, been found with every pair of liquids capable of forming persistent emulsions hitherto examined.

13. The persistence of many emulsions is therefore determined largely, among other factors, by the presence of solid or highly viscous matter at the interfaces of the two liquids. Direct measurements of the various surface tensions concerned are not available, but the close resemblance of the phenomena to those occurring at a free surface, points to the view that accumulation of solid matter at the interfaces of the above emulsion-pairs occurs because the "surface-energy" is thereby diminished.

14. Numerous precipitations of colloids from their solutions by chloroform, ether, carbon bisulphide, and amyl-alcohol, are attended by precisely similar phenomena at the interfaces of the liquids concerned, and appear to be brought about in exactly the same way.

15. The suggestion that the observed surface accumulations must be attributed to the diminution of the "superficial energy" thereby produced, is strongly supported by a series of experiments made with watery solutions containing equal quantities of two substances each of which by itself forms "mechanical surface aggregates." In such mixtures there has invariably been preferential accumulation of one substance to the more or less complete exclusion of the other from the mechanical surface aggregate obtained. Thus—

Saponin	>	Egg-albumin.
Bile-salts	>	Saponin.
,,	>	Soap.
,,	>	Gamboge.
,,	>	Egg-albumin.
,,	>	Sulphur.
Egg-albumin	>	Carmine.

If the dissolved substances thus mixed exert no chemical action upon each other, such preferential accumulation is not only explicable, but, taking only surface-tension considerations into account, is theoretically essential when one substance produces a greater diminution of the surface energy than the other. In actual practice, however, the phenomena are complicated by differences in diffusibility and rate of resolution, and by limitation of independent mobility of the "dissolved" particles due to their mutual cohesions and adhesions.

16. It has been found also that bubbles blown from mixed solutions of two substances, each of which by itself forms bubbles presenting recognisable and well-marked

differences of character, behave precisely as if they have been blown from a solution of one of these substances only, and this is always the one which in a mechanical surface aggregate made from the mixed solution is found to have more or less completely excluded the other, *e.g.* :—

Saponin > Egg-albumin.
Bile-salts > Saponin.
,, > Egg-albumin.
Egg-albumin > Carmine.

17. The fact that the introduction of alcohol (and of other liquids of low surface-tension) into many solutions which show the above described surface phenomena, frequently deprives those solutions of their superficial viscosity and of their power of forming bubbles or of yielding mechanical surface aggregates, would seem to be explicable by similar considerations, *i.e.*, as due to preferential accumulation of alcohol to the exclusion of the suspended or dissolved solid.

18. Various hitherto obscure phenomena find their explanation in the facts observed, *e.g.* :—

i. The ready formation of a "skin" on hot milk exposed to evaporation is explained by (*a*) the presence of a delicate skin or pellicle on the free surface even of cold milk or of caseinogen solutions not exposed to evaporation; (*b*) the presence of a similar pellicle at the inter-faces between caseinogen solutions and pure neutral olive oil or butter-fat.

The existence of a proteid "haptogen-membrane" around the cream-globules of milk cannot any longer be doubted, and their *rôle* in contributing to the ready formation of a thick skin on hot milk, as first demonstrated by Hertz and Jamison (*vide Journ. of Physiol.*, London, 1901, vol. xxvii., p. 26), finds a complete explanation. The apparently contradictory observations of Rettger (*vide Amer. Journ. of Physiol.*, May, 1902), demonstrating the possibility of obtaining very delicate skins by heating caseinogen and other solutions, although free from fat globules, appear to be due to the dehydration and thickening by evaporation of the surface pellicles present on such solutions even in the cold.

ii. The homogeneous "Grenz-membran" described by Bütschli (and the optical homogeneity of thin films referred to by Hardy) in various coagulated or dehydrated colloids, is the above described membrane of solid colloid formed at an air or other appropriate surface.

iii. The high pressure required to force solutions of saponin and albumin through capillary tubes when bubbles of air are present is largely due, among other factors, to the presence of solid membranes around the air-bubbles, and the increased resistance to de-formation brought about. As Plateau showed, the resistance offered is enormously greater than that of water containing similar air-bubbles. (*Cf.* air-embolism in the blood-capillaries of a mammal).

iv. The failure of proteids and other colloids in solution to pass through fine filters without considerable loss is largely due to the formation of surface membranes and mechanical coagula upon air, grease, or other suitable surfaces in the pores of the filter.

19. The following table indicates some of the substances whose aqueous solutions or suspensions have shown evidence of the accumulation of solid or highly viscous matter on their free surfaces, either by (1) yielding "mechanical surface aggregates"; (2) intense special superficial viscosity; or (3) forming persistent bubbles.

It will be seen that there is a very considerable parallelism in the three phenomena. Exact parallelism could not be expected, since the different physical properties of the surface accumulations must necessarily affect the phenomena in different and highly complex ways. Special superficial viscosity has only been recorded when very intense, and all minor degrees have been ignored, since the presence of dust, &c., in minute quantity may, as has been shown by Lord Rayleigh (*Roy. Soc. Proc.*, 1890, vol. xlviii., pp. 127—140), produce some "superficial vicosity," and it has been practically impossible entirely to exclude such contamination. Power to form persistent bubbles has been shown by either :—

i. The possibility of blowing 2-inch bubbles.
ii. The formation of a froth.
iii. The formation of small bubbles which last in closed vessels at least thirty minutes.

In all cases the substances employed have been of the greatest attainable purity, the de-soluted solids have been shown to consist of the same material as that in solution or suspension, and numerous control experiments have been made.

Aqueous solutions or "suspensions" of—	Solid mechanical surface aggregates.	Intense superficial viscosity.	Persistent bubbles.
Proteids of egg-white—			
1 in 10 to 1 in 100,000	+	+	+
1 in 1,000,000	+	−	−
1 in 10,000,000 ..	−	−	−
Crystalline egg albumin ..	+	+	+
Serum proteids	+	+	+
Serum albumin	+	+	+
Fibrinogen	+	+	+
Alkali albumin	+	+	+
Acid albumin	+	+	+
Caseinogen in clear solution in Na_2CO_3 solution	+	+	+
Gelatin	+	+	+
Primary albumose	+	+	+
Secondary albumose ..	+	+	+
Peptone (from peptic digestions) soluble in absolute alcohol	+	+	+
Muscle proteids	+	+	+
Plant vitellin from lentil seeds	+	+	+
Sodium palmitate	+	+	+
Sodium oleate	+	+	+
Methyl-orange	+	+	+
Orange G	+	+	+
Spiller's purple	+	+	+
Saponin—			
1 in 100 to 1 in 100,000	+	+	+
1 in 1,000,000	+	+	−
1 in 10,000,000 ..	−	−	−
Sapogenin	+	+	+
Digitalin	+	−	+
Ferric acetate	+	+	+
Cupric acetate	+	+	+
Colloidal ferric hydrate ..	+	+	+
Carmine	+	−	+
Colloidal sulphur	+	−	+
Bile-resin (dysylsin) ..	+	+	+
Bile salts	Viscous gum	−	+
"Caramel"	+	+	+
Gum mastic	+	+	+
Shellac	+	+	+
Starch mucilage (½ %) ..	+	−	−
Gamboge, 1 in 1000 ..	+	−	+
Gamboge, 1 in 1,000,000.	+	−	−
"Flowers of sulphur" ..	+	−	+
Animal charcoal	+	−	+
Quinine bisulphate (solution)	−	−	−
Quinine bisulphate (excess in suspension)	+	−	+
Quinine solution	+	−	+
Picric acid (solution) ..	−	−	−
Picric acid (excess in suspension)	+	−	+
Salicylic acid (solution) ..	−	−	−
Salicylic acid (excess in suspension)	+	−	+

ON THE RADIO-ACTIVE EMANATION IN THE ATMOSPHERIC AIR.*

By J. ELSTER and H. GEITEL.

(Concluded from p. 32).

II.

On the Dependence of the Radio-activity of the Free Atmosphere on the Meteorological Elements.

By J. Elster.

From December 15, 1901, to the end of December, 1902, we have determined on 155 days altogether the radio-activity of the air at our dwelling place by the method specified by us and already accurately described (*Physikal. Zeit.*, 1902, iii., p. 305). In this method, the metal wire 10 m. long and about 1 m.m. thick, was freely stretched, with ebonite insulators and sodium drying, at a height of about 2 m. above the ground, from one corner of the house to another at right angles to it; a short moistened string connected it with the inner coating of a Leyden jar; the constancy of the charge of the wire was controlled by means of a high-tension electroscope connected to it; the time of exposure amounted always to two hours. It was, however, not always possible for us to watch continually the arrangements for charging the Leyden jar (inductor, water influence machine, high-tension dry pile), but care was taken that the potential of the stretched wire did not exceed 2800 volts, and did not fall below 2000 volts.

Some uncertainty was attached to the numbers obtained by us, for the reason, which became specially obvious later, that the induced radio-activity is more dependent upon the potential of the wire during the exposure than we believed originally. The theory then put forward by us (*cf.* the record of last year's session), that for thin wires the induced radio-activity is practically independent of the potential of the wire while it is being rendered active in free air, so long as this exceeds 2000 volts, can probably not be maintained without limitations, according to more recent developments. In future measurements it will be better to aim at charging the wire to exactly the same potential from day to day than at working with perfectly constant potentials while the activity is being excited in the wire.

After the activity had been excited, the wire was wound on a cylinder of metal gauze, which was introduced (fitting closely to the wall) into the protecting cylinder of our leakage electrometer—closed for this purpose underneath also, except for a central opening. As before, we put the activity of the air = 1, if, after two hours' exposure, a metre of the wire which was rendered active lowered the potential of the leakage substance by 1 volt in one hour. Before each measurement we determined the loss of tension which the leakage substance charged to a potential of about 260 volts experienced in the course of an hour in the closed protecting cylinder by the natural ionisation of the air, and then took this amount into account in the final measurement. To show the method of observation and calculation employed, we give here the record of one of these determinations:—

Excitation of Activity on June 27, 1902.—Cloudiness, 1; high transparency of the air; leakage of electricity, 1·6 per cent; barometer, 763·6; temperature, 26·6° C.; direction and strength of wind. N.E.$_4$; wire of 1—3 μ exposed with the high tension dry pile; potential of the wire, 2500 volts.

I. *Control Experiment, before the Wire is rendered Active.*

Initial potential .. .. .. 20·2; scale div. = 264 volts.
Potential after 15 minutes . 19·9; ,, = 255 ,,

Loss of tension of leakage substance in fifteen minutes = 9 volts, thus in one hour = 36 volts.

II. *Experiment after Wire is rendered Active.*

Initial potential .. .. .. 22·0; scale div. = 264 volts.
Potential after 10 minutes . 10·2; ,, = 201 ,,

Loss of tension of leakage substance in ten minutes = 63 volts, thus in one hour = 378 volts.

Effect of wire 10 m. long alone = 378 − 36 volts = 342 volts.

Effect per metre = $\frac{342}{10}$ = 34·2 volts. Thus A = 34·2 volts.

The meteorological data we took from the information given by the Meteorological Station at Brunswick, the director of which, Herr Klage, most kindly placed them at our disposal.

When specially high or low values of these activity numbers (A) were found, they were often checked many times in the course of the day, and we consider them accurate enough to be used for deducing definite results from the total material accumulated, and hope that thus we shall lead to a repetition of our experiments in other places.

We give here the tables of the means for the months, A (mean), adding the maxima and minima observed, A (max.) and A (min.), as well as the number of days, *n*, on which observations were taken.

Table I.

	1901.	1902.										
Months	XII.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
A (mean) ..	28	14	13	20	16	24	32	—	15	16	9	22	22
A (max.) ..	50	47	40	40	32	44	64	—	40	32	18	31	34
A (min.) ..	17	4	5	5	9	6	18	—	6	5	4	4	17
n	16	20	19	11	13	10	11	—	18	13	11	8	5

Remarks.—The observations are not given for the month of July, nor for days with plentiful atmospheric deposition.

It may be at once concluded from this table that the amount of radio-active emanation contained in the free atmosphere is subject to remarkably great variations. The extreme values are to one another as 16 to 1 (absolute max. = 64; absolute min. = 4). The mean value for the year is 18·6.

To decide the question whether the number of free ions present in the air and their mobility have any influence on the magnitude of the activity number, we have also determined the percentage leakage of electricity, *a*, on ninety-six days altogether, and used the latter as a standard for both quantities. We then divided the coefficients of leakage obtained into nine groups, and associated with the mean of each group of the *a* the mean of the A belonging to it. Thus we got Table II.

Table II.—*Dependence of the Radio-activity of the Air on the Leakage of Electricity.*

Group No. ...	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
No. of observ...	12.	14.	19.	9.	11.	10.	9.	9.	3.
a (per cent)	0·80	1·1	1·4	1·6	1·7	1·9	2·1	2·4	3·3
A (mean)..	17·1	14·5	16·1	18·1	14·0	17·4	17·7	28·7	29·7
A (max.) ..	40	43	41	32	22	40	64	47	40
A (min.) ..	5	6	5	7	8	5	6	11	21

We were surprised to find that, as shown by this table, for a percentage leakage of 0·8 to 2 the mean values of A differed by only a few units, while the maxima and minima seem to be irregularly distributed through Groups I. to VII. A considerable rise in the values A (mean) and A (min.), compared with the previous numbers, first appeared in the last two groups, unfortunately containing only a few observations.

Against the existence of a direct connection between the radio-activity of the air and the coefficients of leakage may be adduced the fact that the greatest amounts of activity are excited during fogs; the values then obtained exceed or closely approximate to the mean for the year, while the leakage of electricity is known to be small when the air is misty. In Table III. some observations relating to the activity excited in foggy air are collected.

* Aus der Denkschrift der Kommission für luftelektrische Forschangen, Munchen, 1903.

TABLE III.—*Radio-activity of the Air in Fogs.*

Date.	A.	Remarks.
20/XII./01	25	Wet fog.
23/XII./01	27	„ „
13/II./02	41	Light ground fog.
1/III./02	22	Damp fog.
15/XI./02	31	Thick mist.
15/XII./02	16	Fog; hoar-frost.
22/I./03	45	Thick ground fog.

On five days, not included in the table, the activity numbers lay between 4 and 12; thus the foggy air was never *inactive*. In any case it follows from these observations that the conditions in free air are much more complicated than in closed subterranean spaces, in which the conductivity of the air is closely connected with the amount of radio-active emanation.

The temperature of the air also appears to have a decided influence on its radio-activity. If the values of A are grouped together for temperatures above 0° and below 0°, the mean value of A for 136 observations at temperatures above 0° is 18, and for 19 observations at temperatures below 0° A = 26. Rutherford, also, on repeating our experiments in Canada, found that on cold frosty days the activity of the air is specially high.

As regards the direction of the wind, we found that with winds blowing from the continent, the values of A are on an average higher than with those which blow from the sea. (*Cf.* Table IV.)

TABLE IV.—*Dependence of the Radio-activity of the Air on the Direction of the Wind.*

Wind directly from—	A (mean).	A (max.).	A (min.).	*n*.
S.	22	50	6	14
N.	15	23	4	4
E.	22	64	6	18
W.	12	32	5	23

The remarkably high and often quite irregularly occurring maxima of A were observed mostly with purely southerly or easterly winds, or with those winds which had a southerly or easterly component.

Whether the above theory as regards the direction of the wind always holds good must be ascertained from further experiments, and by using a wire which is exposed at a place where it is equally accessible to winds from all directions, which was not possible for us. The house protected it from currents of air coming directly from the north and east.

For this reason the influence of the strength of the wind is very difficult to ascertain from the materials collected by us. Moreover, out of the 155 observations made, 111 were made when the wind strengths were 4, 5, and 6. Fourteen observations only were made when the strengths were 1 and 2, for which the mean value is A = 23, while for the 9 observations with strengths 7 and 8 A (mean) is 13·5. These numbers appear to show that the activity is higher the more stagnant the air is over the earth's surface. The large values of A found for misty air point to the same conclusion, for at our place of residence fog is almost always associated with complete lack of wind. But it is also quite possible that an optimum of air movement exists.

The radio-activity of the air undoubtedly depends on the height of the barometer (*cf.* Table V.).

TABLE V.—*Dependence of the Radio-activity of the Air on the Height of the Barometer.*

Mean bar. height	740 m.m.	750 m.m.	760 m.m.	770 m.m.
A (mean)	23	19	17	13
Number, *n* ..	23	56	68	8

This influence of the height of the barometer becomes intelligible when it is remembered that we discovered that the amount of radio-active emanation in that part of the atmosphere which is beneath the earth's surface is abnormally high as compared with that of the air above the earth's surface. A lowering of the atmospheric pressure must thus cause the air of the ground to be drawn up from the capillaries of the earth into the atmosphere, and hence the activity is increased. So long as the penetrability of the earth's surface is not altered, we must expect that every decrease of atmospheric pressure will be accompanied by an increase of the radio-activity in the free atmosphere. But this is not always the case. If at the same time events occur by which the penetrability of the capillaries of the earth is affected, as, for example, alterations in the position of the underground water, or such changes as partly withdraw from the air the radio-active emanation present in it, *e.g.*, abundant precipitation,* a rise of activity must not be expected with a falling barometer.

To prove these results which naturally follow from the radio-activity of the air of the ground, we resumed the experiments from February 14th to March 29th of this year, taking a measurement daily.

In Table VI., $-\delta$ B denotes the fall of the barometer; $\pm\delta$ A the increase or decrease observed at the same time in the activity number. In the given period, a steady fall of the barometer in the course of two or more successive days took place fourteen times. On looking at the table we see that if we except some anomalies observed after the fall of dust, which was known to occur on February 22nd, in ten cases with decreasing atmospheric pressure, an increase of radio-activity occurred, and only in four cases the alteration in the value of A took place in the opposite direction. In these measurements, in order to shorten the time of observation, the wire which was to be rendered active was only exposed for thirty minutes; for which reason for the given period of time the differences between A (max.) and A (min.) are much smaller than if the exposure had lasted two hours. The values of A now ranged from 4 to 24 as compared with 4 and 64 in the earlier measurements.

TABLE VI.—*Summary of the Increase of Activity with Falling Barometer.*

Interval. From—	Interval. To—	$-\delta$ B.	δ A.	Remarks.
18/II.	23/II.	−13·5	+14·6	On the 22nd a transitory alteration in the opposite direction, after fall of dust and rain.
24/II.	25/II.	−1·5	+4·8	
25/II.	26/II.	−4·7	−13·8	Alteration in the opposite direction. On 26th, 7 o'clock a.m., it was raining; the second day was rainy.
26/II.	28/II.	−10·7	+12·7	
1/III.	3/III.	−19·9	+3·0	
4/III.	5/III.	−0·6	+3·9	
9/III.	10/III.	−5·0	−8·1	Alteration in the opposite direction.
10/III.	11/III.	−0·4	+6·9	
14/III.	15/III.	−3·7	+5·4	
15/III.	16/III.	−3·9	−6·7	Alteration in the opposite direction.
17/III.	18/III.	−6·2	+6·8	
21/III.	23/III.	−7·8	+10·1	
23/III.	24/III.	−1·3	−19·7	Alteration in the opposite direction, after a heavy fall of rain at night.
25/III.	27/III.	−6·8	+13·5	

In the course of the month of July, 1902, we performed activity experiments at other places; Geitel in the first half of the month at Clausthal in the Hartz, and in the second half on the shore at Zinnowitz on the Baltic Sea, while

* According to C. T. R. Wilson's and McLennan's researches, rain and snow are active by induction. Thus the suggestion here made is probable (*cf.* J. C. McLennan, "University of Toronto Studies Physical Science," Series 1903, No. 1, p. 12)

Elster performed similar experiments from July 6th to 31st on the north Frisian Island, Juist.

Geitel's results, as far as they extended to experiments with the air of cellars, have already been given in the preceding part of this communication.

For the experiments in Juist we used the portable apparatus arranged by us for the determination of the radio-activity of the air (*Physikal. Zeit.*, 1902, iv., No. 4, p. 2), consisting of the leakage electrometer, the high-tension electroscope, the high tension dry pile of about 2500 volts, and two bell-shaped wire-holders with ebonite insulators, and sodium drying. This apparatus, we might mention, has proved quite trustworthy throughout, even in damp weather, and with the air filled with salt dust, we could charge the wire system a short time after connecting to the negative pole of the pile, so that the high tension electroscope showed 2200 volts, and little sparks could be drawn from the wire.

The measurements were not taken on the beach itself, but at an open space in the village. The wires were insulated, and stretched between two bamboo rods at a height of about 3 m. above the earth's surface. From the stretched wire a conductor led at right angles to the negative pole of the pile, which in hot weather stood on a little table in the open air in the sun; in unsettled weather, on the other hand, it was placed in a house; in this case the wire was led in through the open window.

Measurements were taken on twenty-one days altogether. The mean value was A (mean) = 5·2; the maximum, A (max.) = 15·8, was observed during a N.N.W. storm and squally weather on 11/VII.; the minimum, A (min.) = 1·6 on 25/VII. when the wind was light S.W. and the sky cloudy.

If we compare with these the values obtained in Wolfenbüttel from June 20th to July 1st, and again from August 1st to September 1st under exactly the same experimental conditions (in these periods of time the high tension dry pile was exclusively used):—

June: A (mean) = 27, A (max.) = 34, A (min.) = 16; $n = 5$.

August: A (mean) = 15, A (max.) = 40, A (min.) = 6; $n = 18$.

We must conclude that the sea air contains only about one-third as much active emanation as the air of Wolfenbüttel. Nevertheless, the leakage of electricity was certainly not less than with us. The mean of 21 (double) observations was $a+ = 1·23$, $a- = 1·89$; thus a (mean) = 1·56 as against 1·43 in Wolfenbüttel in June and 1·35 in August (*Wien. Bed.*, 1902, vol. iii., II. A., p. 961); thus the mean percentage leakage in July with us may be given very approximately as 1·4.

This circumstance that the sea air conducts as least as well as, but nevertheless contains less radio-active emanation than the air over the interior, certainly points to the fact that other sources of the ionisation of the atmosphere exist than the penetration of the air of the ground. The few observations which Geitel took at Zinnowitz on the Baltic Sea led likewise to lower activity numbers for the free air than in Wolfenbüttel; a measurement in Clausthal gave A = 33.

The small radio-activity of the air over Juist shows also that activities excited by the natural electric field of the earth are far less decided than with us. In a stiff sea breeze it is easily possible to hold a kite for hours at a very considerable height above the earth's surface. Such experiments were carried out many times on days with an electric fall of 200 to 400 volt/meter, which often occur in Juist. The activity of the upper end of the kite string was, however, very small. On 5/VII. A was 1·6; on 8/VII., A = 2; on 19/VII. A was only 0·4; and on 22/VII. A was 2·3. On using a string moistened with sea-water on 27/VII. A was 3·7. These values are of the same order of magnitude as those obtained with earthed wires stretched horizontally at about 10 m. above the surface, with a fall of potential of about 100 volt/meters (*cf.* our last year's report).

ON THE

MANUFACTURE OF SULPHATE OF COPPER.*

By GUSTAVE GIN.

The usual method adopted for the manufacture of sulphate of copper depends on the direct attack of copper or binoxide of copper by sulphuric acid.

This method is good when the production of sulphate of copper is simply the consequence of other metallurgical operations of greater importance; for example, in the separation of the precious metals alloyed with the copper.

In such cases, the cementation of the cuprous solutions logically follows the principal operations, and it is natural to use this cement copper for the production of the sulphate of this metal.

But it must be remarked first that the direct attack of cement copper requires the use of heat, and involves a considerable loss of sulphuric acid given off in the form of sulphurous acid, according to the reaction $2SO_4H_2 + Cu = SO_4Cu + SO_2 + 2H_2O$.

Further, cement copper is always impure, and hardly ever contains more than 60 or 70 per cent of pure copper, and we can only obtain an equally impure sulphate of copper by direct attack, while trade requirements now limit the maximum proportion of impurities to only one and a half or two per cent.

Thus we are obliged first to proceed with the purification of the cement copper by melting, refining, and granulation, and to avoid the loss of the reagents we then oxidise the cement copper by roasting in muffle furnaces. This latter operation is costly, as it causes the disengagement of abundant fumes carrying with them considerable quantities of the metal; this loss is only partially obviated by the construction of dust chambers and condensation towers, in which the solid matter escaping from the furnaces is collected.

It is to remedy these imperfections that I have endeavoured to find a process for the commercial production of sulphate of copper, starting directly from the sulphurised ores, or from poor mattes, and without submitting the metal to any intermediate preparation.

Direct Method for the Sulphating of Mattes or Ores.

The ore or matte, suitably broken up, is subjected to an oxidising roasting in a muffle furnace, sufficiently prolonged to transform the whole of the sulphide of copper into oxide or sulphate.

This result is only attained after the complete dissociation of the sulphate of iron, and the partial decomposition of the sulphate of copper formed. In practice we may consider that there is no more copper left in the form of sulphide when four-fifths of the sulphate of copper are transformed into binoxide.

When the operation is complete, we remove the ore from the sole of the muffle furnace to the floor of a cooling chamber, through which the sulphurous gases from the oxidisation of the sulphur and the dissociation of the sulphates are passed after mixing with a suitable amount of air.

These gases move with the ore, which is gradually shovelled towards the other end of the cooling chamber, opposite to the roasting furnace.

On account of the lowering of the temperature, a series of chemical changes is produced between the ore and the sulphurous gases, similar to those observed in Sainte-Claire Deville's *hot and cold tube*.

Thus we bring into the presence of the calcined ore a mixture of sulphurous anhydride and air, which, by the well-known catalytic action of peroxide of iron and sulphate of copper, forms sulphuric anhydride, which at a lower temperature transforms first the oxide of copper, and secondly, the peroxide of iron into sulphates. It is necessary to observe that on account of its higher tension of dissociation at the temperatures through which the ore

* A Paper read at the Fifth International Chemical Congress at Berlin, 1903 (Section II.).

successively passes, ferric sulphate cannot be formed until after the sulphate of copper.

The transformation of the sulphurous anhydride into sulphuric anhydride begins to take place as soon as the temperature falls below 750°, and the speed of the reaction appears to be at its highest between 550° and 600°.

It is best not to let the temperature fall below 500° to prevent the formation of ferrous sulphate by the reaction $Fe_2O_3 + 2SO_2 + O = 2SO_4Fe$.

Finally, it is necessary to remark that above 500°, only basic ferric sulphates can be formed ($S_2O_9Fe_2$,SO_6Fe_2).

An idea that has been entertained by several inventors is that of limiting the reactions entirely to the sulphating of the copper, leaving the peroxide of iron intact, the surplus sulphurous gases being directed into an apparatus for the regeneration of sulphuric acid (lead chambers or an arrangement for oxidation by contact).

However, this regulation of the reactions is impossible, and I found that it is advantageous to produce, on the contrary, the largest possible quantity of basic ferric sulphate, which serves ultimately as the vehicle for carrying the sulphuric acid to other portions of the ore. The sulphated ore submitted, as has been said, to a methodical lixiviation, gives hot concentrated solutions, which are digested hot with ore that has been roasted sweet, and contains, consequently, the whole of the copper in the state of binoxide. The ferric sulphate sulphates the copper, while the iron is precipitated in the state of peroxide according to the exothermic reactions :—

SO_6Fe_2 dis. + CuO ppt. =
= SO_4Cu dis. + Fe_2O_3 ppt. (+45·9 cals.).

$S_2O_9Fe_2$ dis. + 2CuO ppt. =
= $2SO_4Cu$ dis. + Fe_2O_3 ppt. (+31·2 cals.).

Thus we obtain solutions of sulphate of copper relatively pure, and which are treated as we shall describe further on.

I may add that this method of sulphating is not indispensable, and that any method of roasting may be used if it is pushed to complete oxidation with subsequent sulphating by the wet method, as the purification we are about to describe completely realises the separation of the sulphates of iron and copper.

Purification of Solutions of Sulphate of Copper.

The impurities contained in raw solutions of sulphate of copper can be always reduced by means of separate crystallisations, to the presence of iron in the states of ferric and ferrous sulphate.

Then, to get the pure sulphate of copper, the ferric sulphate is reduced to the state of ferrous sulphate, and subsequently separated from the sulphate of copper by purely physical means, utilising the variations of the respective solubilities of the two salts at a high temperature.

From the researches of M. Etard on saturated solutions at high temperatures, it appears that the coefficient of solubility of pure sulphate of copper reaches a maximum at about a temperature of 100°, and then decreases very slowly. The solubility of ferrous sulphate is at its highest a little below 100°, and then diminishes rapidly, becoming *nil* at a temperature below 160°.

If we put the two salts into water simultaneously, we observe that their respective solubilities follow laws entirely different to those corresponding to solutions of the sulphates taken separately. The solubility of ferrous sulphate first increases with the temperature, more rapidly than that of sulphate of copper; then the variations change in direction, and above 100° the respective solubilities again take the course which characterises the isolated salts, so that at about 160° the whole of the sulphate of copper remains in solution, while the ferrous sulphate is completely precipitated.

From these observations I have devised the method for the separation of the two salts which I will now describe :—

The ore, sulphurised or otherwise, or the matte from which the sulphate of copper is to be extracted, is submitted to a preliminary treatment by which the metallic sulphides are transformed into sulphates, then to a methodical lixiviation, so as to obtain, as I have described above, solutions of sulphates, as saturated and as hot as possible, containing sulphate of copper and a more or less high proportion of sulphate of protoxide of iron.

If the solution still contains a little ferric sulphate, a current of sulphurous acid is passed through it; this reduces the peroxide salt, and transforms it into ferrous sulphate.

The solution, maintained almost at a boiling temperature, is then filtered, and contains only sulphate of copper and sulphate of protoxide of iron. By means of a pump, it is forced into a tubular copper boiler, in which it is heated until the manometer shows a pressure of 10 kilogrms.; that is to say, to a temperature of about 180°; at this temperature the sulphate of protoxide of iron can no longer remain in solution, while the sulphate of copper is still very soluble.

We may remark here that it is advantageous to use concentrated solutions, but without allowing this concentration to reach the maximum saturation point for sulphate of copper, or a little sulphate of copper would be precipitated at the same time as the sulphate of protoxide of iron.

A concentration of 350 to 400 grms. of sulphate of copper per litre of solution is favourable to the separation.

It is necessary to have an active circulation in the tubes, to prevent the formation of deposits adhering to the sides of the tubes. Still, if such deposits are formed, they are easily removed when the boiler is not in use, by a simple washing with cold water.

The usual pressure is then used to drive the solution into a filter-press, of which the hollowed plates are heated by steam at 10 kilos. pressure, to delay the cooling of the solution as much as possible.

The cloudy liquid penetrates the cloths, where it leaves the suspended ferrous sulphate, while the solution of sulphate of copper runs in a clear stream into the crystallising vat. When the limited pores of the filter cloths are filled with the precipitate of ferrous sulphate, the operation is arrested, and the solution to be filtered passed through another filter-press.

The circulation of the steam being arrested, the plates are washed with pure water, which rapidly dissolves the sulphate of iron.

The solutions thus obtained are passed into a special reservoir for crystallisation.

The filter-press being now perfectly cleaned, it can be used at once for a fresh filtration, the operation being made continuous by the alternate use of two filter-presses.

We may also remark that the filter-press itself being cleaned by simple washing, there is no necessity to remove the plates except for the purpose of renewing the worn-out cloths.

The solutions of sulphate of copper are passed into wooden crystallising vessels lined with lead. Strips of lead are suspended in these vats, and the crystals of sulphate of copper attach themselves to them.

When the crystallisation is complete, which takes place in about five or six days, the mother-liquors are drawn off, and the crystals drained and dried in a centrifugal machine before packing.

The mother-liquors come again into circulation for the production of fresh solutions.

METEORIC DUSTS, NEW SOUTH WALES.*

By Prof. A. LIVERSIDGE, LL.D., F.R.S., University of Sydney.

(Concluded from p. 45).

The following articles and letters upon atmospheric dust and dust storms from other parts of the world are not only interesting, but they throw a great deal of light upon the subject of meteoric or atmospheric dust and dust phe-

* Read before the Royal Society of N.S. Wales, September 3, 1902. From the *Journal and Proceedings of the Royal Society of N.S. Wales*, vol. xxxvi., p. 241.

nomena generally as experienced in Australia. Many more examples could have been given, especially if the meteorological pubications had been laid under contribution; those given are some of those noted down in the ordinary course of reading.

Dust Atmosphere of China.—J. P. O'Reilly, Dublin, in a letter to *Nature*, January 17th, 1884, quotes from von Richtofen's work upon China, in reference to the dust atmosphere so characteristic of Central Asia, and more particularly of the *loess* district :—"Even during complete calms the atmosphere is often for many days yellow and opaque. The view is completely hemmed in, and the sun appears merely as a dull bluish disk."

More markedly is this character presented by these peculiar dust storms so well known to travellers visiting Tien-tsin and Pekin, and even more so to those who travel in the interior of the N.W. provinces of China. The wind then blows from Central Asia and everything becomes covered with a fine yellowish dust.

"In Schensi, where the air is rarely clear and transparent, the whole landscape has a yellow tint; streets, houses, trees, crops, and even the traveller one meets on the road, and the air itself, one and all, are yellow coloured" (see also Johnson's "Journey to Ilchi, the capital of Kotau," *Royal Geographical Society*, 1867, p. 5).

A writer in *Nature*, August 12th, 1886, p. 348, quoting from an article in the *American Meteorological Journal*, upon the dust storms of Pekin, says:—"These occur in the dry season, especially in the winter and early spring; they come on at irregular intervals, perhaps six or eight times in the season, and last about three days. The wind is W. or more often N.W. and blows fresh or high. The dust extends eastward from Pekin to the sea, and south-eastwards it regularly descends as far south as the Yellow River, and sometimes to Shanghai, 10° of latitude away."

The writer of the paper says this vast quantity of dust must come from the great deserts of Mongolia. He also refers to the variations in the barometer and thermometer accompanying the storms, and to the obscuration of the sun, which was set in a ring.

Dr. H. B. Guppy, in *Nature*, June 9th, 1881, says that in the spring of 1878 his attention was directed to the dust-winds which are of frequent occurrence in the valley of the Yang-tse, in the warm and dry season of the year. According to his observations at Hankow, they sometimes had the appearance of a dense mist, and at other times the air seemed to be penetrated by a fine haze, and in all cases a fine and impalpable dust was deposited, which was with difficulty excluded from the interior of the houses. Their duration lasted from a few hours to two days. He concluded that they are not local phenomena from the fact that one was experienced simultaneously from Hankow to Chinkiang, a distance of nearly 450 miles. The dust resembles the loess of the alluvial plains of the Yang-tse, and is generally made up of siliceous or calcareous particles from 1/1000 to 1/500 inch in size, and vegetable débris. From a study of the meteorological and electrical conditions of the atmosphere, he does not think they are due to sudden breezes.

Prof. S. P. Langley, of the Allegheny Observatory, Penn., in speaking of the red sunsets seen all over the world, says (*Nature*, January 31st, 1884) "we know of but two likely causes: one is the advent of an unusual amount of meteoric dust. While something over ten millions of meteorites are known to enter our atmosphere daily, which are dissipated in dust and vapour in the upper atmosphere, the total mass is small, compared with the bulk of the atmosphere itself, although absolutely large. It is difficult to state precisely what this amount is . . . approximately not greatly more than 100 tons, nor greatly less than 1000 tons a day.

"Taking the largest estimate as still below the truth, we must suppose an enormously greater accession than this to supply a quantity sufficient to produce the phenomenon in question; and it is hardly possible to imagine such a meteoric inflow unaccompanied by visual phenomena in the form of "shooting stars," which would make its advent visible to all. Admitting then the possibility of meteoric influence, we must consider it to be nevertheless extremely improbable. There is another cause, which I understand has been suggested by Mr. Norman Lockyer—though I have not seen his article—that of volcanic dust."

Prof. Langley then speaks of the dust present in the apparently clear air of the upper parts of Mt. Etna, surrounded by snow field and deserts of black lava, yet the telescope showed that the air was filled with minute dust particles, which evidently had no relation to the local surroundings, but apparently formed a portion of an envelope common to the whole earth.

In 1881, Prof. Langley was on Mt. Whitney, Southern California, with an expedition from the Allegheny Observatory, where from a height of 15,000 feet they looked down upon a kind of level dust ocean, invisible from below, but whose depth was six to seven thousand feet. The colour of the light reflected from this dust was clearly red, and it stretched in every direction as far as the eye could reach, although there was no special wind or local cause for it. It was evidently like the dust seen in mid ocean from the Peak of Teneriffe; something present all the time and a permanent ingredient of the earth's atmosphere.

Mr. Clarence King, Director of the U.S. Geological Survey, thought that this upper dust was probably due to the "loess" of China having been borne across the Pacific and quarter of the way round the world. We were at the top of the continent, and the air which swept by us was unmingled with that of the lower regions of the earth's surface. Even at that great elevation the dust was perpetually present in the air, and I became confirmed in the opinion that there is a permanent dust shell enclosing the whole planet to a height certainly of about three miles, and probably to a height even greater. The meteorites which are consumed at an average height of 20 to 40 miles must add something to this."

E. Metzger, in a letter to *Nature*, Jan. 17, 1884, p. 261, draws attention to the presence of particles attracted by the magnet in the sand dunes near Scheveningen.

Some atmospheric dust collected at Klagenfurt, Carinthia, after a rain of mud, which had taken place on October 14, 1885, was found to consist of minute crystalline granules and flakes of quartz, opal, orthoclase, biotite, phlogopite, pyroxene, amphibole, mica, talc, kaolin, chlorite, rutile, anatase, zircon, tourmaline, ferruginous clay, spinel, magnetite, pyrites, magnetic pyrites, calcite, magnesite, dolomite, and apatite; metallic iron could not be found. Diatoms, &c., were present, together with a few carbonaceous or carbonised substances, such as the spores of fungi, filaments of algæ, &c., silicified membranes of parenchymal cellules, and pyritised and silicified spherules resembling pollen. Its reddish yellow colour, resembling the "Passat" dust, may be against its having come direct from the Sahara (Dr. M. Schuster, Imp. Acad. Vienna, January 14, 1886; and *Geol. Mag.*, 1886, p. 122).

In an address delivered to the Royal Meteorological Society, January 15, 1890, Dr. William Marcet, F.R.S., President, quotes from a paper by Dr. Cook in the *Journ. Roy. Meteorological Society*, who says that in India there are some days on which, however hard and violently the wind may blow, little or no dust accompanies it, while on others, every little puff of air or current of wind forms or carries off with it clouds of dust. If the wind which raises the dust is strong, nothing will be visible at the distance of a few yards, the sun at noon being obscured. The dust penetrates everywhere, and cannot be excluded from houses, boxes, and even watches, however carefully guarded. The individual particles of dust appear to be in such an electrical condition that they are ever ready to repel each other, and are consequently disturbed from their position and carried up into the air. Dr. Cook also describes dust columns and dust storms, and the electrical origin of both.

In a letter dated Tokio, April 23, Prof. J. Milne, F.R.S., states (*Nature*, June 29, 1892) that the commander,

Capt. R. Swain, of the S.S. *Yokohama Maru*, gave him a specimen of some dust which fell on the vessel on April 2, when about 95 miles west by south of Nagasaki, at about 6 p.m. The sun appeared quite yellow. The atmosphere was moist, and rendered everything upon the deck of the ship quite damp; the precipitated moisture was yellowish, and as it dried it left an extremely fine powder. For two days previously the wind had been blowing W.S.W., or from China. Nothing was felt in the eyes, and if the ship had not been covered with a yellow powder, the phenomenon would have been regarded as an ordinary but peculiarly coloured fog. . . . The probability is that the material came from the loess plains of China. At Nagasaki, which is 300 miles from the coast of China, a yellow sun was noticed on the morning of the 2nd, and during the day while the dust was being precipitated, the appearance of the atmosphere was compared to a London fog.

On April 1 there was a fall of dust at Nawa, in Okinawa-ken, and on the 2nd dust fell at Gifu. The P. and O. steamer *Verona*, which left Hongkong on April 1, experienced the same phenomenon as the *Yokohama Maru*, the vessel being covered with a fine dust, and there was so much haze that land was not seen until reaching Nagasaki. On April 3, a yellow sun was seen at Yokohama, but I am not aware that any dust was observed. Roughly speaking, it therefore seems that on April 2, at a distance of from 200 to 400 miles from the coast of China, there was a cloud of dust which may have been over 1000 miles and possibly 2000 miles in length. Dr. B. Koto, who examined the dust, tells me that the particles are chiefly felspar, but there is a little quartz and shreds of plants.

An article referring to a shower of dust in connection with snow in Indiana and Kentucky, appeared in the *Monthly Weather Review*, in 1895 (*Nature*, August 29, 1895, p. 419). The dust does not appear to have been the nuclei of the snowflakes, but was intermingled in the air with the snow, and fell during an interval between two snow storms. The examination of a large number of specimens showed that the dust was made up largely of silt, mixed with organic matter. A number of fresh-water algæ were present, though they appear to have been dead and dried for some time. . . . Everything indicated that the material had come from the bottom of some dried up lake, pond, marsh, or river bed. The dust was almost identical with the so-called "loess" formation, which which covers very extensive areas in Illinois, Indiana, Nebraska, and adjoining States, its depth in some places amounting to 100 feet or more. This is interesting, because there is a long standing controversy as to the origin of the "loess" of the north-west. Certain portions of the "loess" formation of Asia are known to be wind deposits, and there is very strong presumptive evidence, now borne out by the examination of the samples of dust, that much of the "loess" of the Western States is also a wind deposit. . . . This light soil is easily raised and carried off by strong winds of the western plains of America; instances have occurred in which six inches of surface soil have been blown away from freshly cultivated fields in the course of a single wind-storm.

J. M. Yates, writing from Davenham, Cheshire (*Nature*, April 1, 1897), says:—"On Tuesday morning, March 22, I noticed on the glass of our greenhouse and on many of the shrubs a sort of red dust. On making enquiries, I found the same thing existed about two miles due west. I collected some, and by the kindness of Messrs. Brunner, Mond, & Co., it was examined in their laboratory. The report says:—The dust showed minute fragments of clayey matter, mixed with quartz; organic matter, such as pollen grains, was absent. The particles are about 0·0001 m.m. in diameter, many of them less. We are surrounded by grass; the soil is clayey loam, without oxide of iron or quartz."

A letter from Augusto Arcimis (*Nature*, April 21, 1898), in reference to the dust shower met with by the *Roslyn Castle*, off the west coast of Africa, describes the phenomenon as experienced at the City of Laguna, Teneriffe. "A light fog was observed from the early hours of the evening of February 15, with a light breeze from the east. During the night it rose to a moderate gale. At about 5 a.m. on the 16th a few drops of rain fell. The wind dropped to a gentle breeze again during the day, from the east. The fog became denser, and the sun pale and feeble like the moon. The drinking water became salty and coloured as by oxide of iron. The dust was grey and extremely fine, and was deposited on every object."

Some brown dust was collected on board the P. and O. S.S. *Sumatra*, during a thunderstorm in the Galita Channel, Mediterranean. Mr. G. T. Pryor (*Nature*, June 29, 1899) found the dust to be an argillaceous and calcareous sand, containing a little organic matter and a few angular grains of quartz.

Prof. Rücker, F.R.S. (now Sir Arthur Rücker), writing from Taormina, in Sicily (*Nature*, March 28, 1901), on March 12 to Prof. Judd, says:—"We have had a rather curious phenomenon here. The sirocco was blowing and the hills were wrapt in mist, but the fog assumed a yellow hue, and the sun, which at times could not be seen through it, was a bright blue. This was caused and accompanied by a copious fall of red dust. Some which I shook off my hat was quite dry, and on looking at it through a low power lens, all the granules appeared to be spherical, except a very few grains of what looked like quartz. . . . This dust also fell at Naples and Palermo in such quantity that the streets looked red, and the people were frightened." Prof. Judd states that under the microscope the dust is seen to be made up of particles of quartz, mica, &c., also frustules of fresh-water diatoms. Prof. Rücker (*Nature*, May 9) estimates the amount from his observation as about seven tons per acre.

Sir Ed. Fry, F.R.S., wrote to *Nature* from Failand, January 28, 1902, describing a fall of reddish or rust-coloured mud or dust, which covered greenhouses, plants, and clothing out to dry; it also fell at Lawrence Weston, about five miles to the N.E., Chewton Priory, some fifteen miles S.E., and Barry Island, some twenty miles W. by S., and on the other side of the Bristol Channel. The above fall was afterwards found to have spread over a large area, since it occurred in Cornwall.

On March 6, there appeared a letter in *Nature* from Mr. Clement Reid, stating that the above fall of red dust in South Wales may have been derived from the Red River dust flats, as he had noticed red dust clouds blown from the flats, and spreading across St. Ives Bay to St. Ives Head, a distance of over three miles. The wind was not a gale, but merely a strong dry east wind.

Gold and Platinum (?) in Meteoric Dusts.—For convenience, the results of the search for these metals are summarised here instead of being given under the headings of the various specimens examined. Minute quantities of gold were met with in two of the dusts examined, viz., from Gundagai and the University tank; that from the University beams also yielded a metal resembling platinum; some of the other dusts have yet to be tested. These metals were especially sought for when grinding and washing the dusts in an agate mortar to separate out the particles of metallic iron, as this is a much more delicate test for minute quantities of gold and platinum in such materials than any chemical test; they were obtained in the form of minute spangles.

The dust from the University beams, collected in 1882, from a portion of the roof some distance from the Chemical Laboratory, and completely cut off from it by several dividing walls and the ceilings, yielded a minute spangle of a white malleable metal, insoluble in nitric acid, even after evaporating the acid down to dryness; hence it appears to be one of the platinum metals. The particle was too minute to admit of applying other wet tests, hence it was not treated with aqua regis.

A dust from Muswellbrook (N.S.W.) yielded particles of a non-magnetic grey metal readily soluble in acid; this was probably zinc or zinc and lead from a galvanised iron

roof. Hartley and Ramage found lead in several meteorites, in volcanic and other dusts, as well as in chimney soots (*Proc. Roy. Soc.*, 1901).

The mud from the University tank, which may have been collecting for 30 years, as the tank had probably never been cleaned out since it was put up, yielded spangles of a yellow malleable metal, insoluble in nitric acid, even on evaporation, and therefore presumably gold; the metallic particles, although visible without a microscope, were very small and insufficient for the application of other tests. There were also present particles of a yellow metal resembling gold, but soluble in nitric acid; these may have been copper or brass (as copper is almost invariably present in meteorites it may have had a meteoric origin); the Menindie dust also contained a yellow metal soluble in nitric acid. The dust from Gundagai yielded yellow malleable metallic spangles insoluble in nitric acid, and therefore presumably gold.

In most cases some of the metallic spangles were visible without a lens; these were separated from the rest of the material left in the mortar by picking them up on the point of a needle and transferring them to a slide for examination under the microscope; under a one inch objective they still looked like gold; the action of the nitric acid was also watched in the same way; some of the soluble ones were seen to dissolve slowly, others quickly, with many minute gas bubbles.

The gold and platinum may or may not be of meteoric origin, but as both metals have been met with in meteorites (an account of the occurrence of gold in meteorites will be given in a subsequent paper), and platinum has apparently been previously found in meteorites (Davidson, *Am. Journ. Sci.*, 1898; Mingaye, "Report of the Dept. of Mines, Sydney," 1898, p. 21), it is not impossible that both the gold and the platinum metal may have had a cosmic source, although it is much more probable that the gold has been wind-borne from some auriferous area, for even the sandstone and shales about Sydney contain traces of gold (A. Liversidge, *Journ. Roy. Soc. N.S.W.*, 1894, pp. 185—188).

Conclusion.

I have quoted what may be considered by some as an unnecessarily large number of accounts of meteoric dusts, dust storms, rains of mud, dry fogs, &c., but I do so because some of the explanations given by different observers do not appear to quite account for the phenomena, and it appears to be desirable that sufficient evidence is needed for each to judge for himself. My own opinion is that the phenomena of dry fogs or haze, of dust-storms, and mud rains are not due to extra-terrestrial causes; I think that the material or dust is mainly made up of débris, inorganic and organic, from the land, and occasionally, as everyone is aware, of volcanic dust; mingled with this undoubted telluric matter there appears to be nearly always a certain amount of extra-terrestrial or cosmic matter, *i.e.*, the dust or débris of meteorites, although in most cases it is very difficult or even impossible to discriminate between the terrestrial and the cosmic dusts.

The presence of cobalt and nickel in the iron of a dust was formerly regarded as a proof of its meteoric origin, but it is now known that both of these metals occur in the metallic iron met with in some rocks, and notably in the telluric irons of Greenland; nickel has also been found in dust from volcanoes, and in the soot from coal smoke, by W. Noel Hartley, F.R.S., and Hugh Ramage (*Proc. Roy. Soc.*, March, 1901, p. 97). They also found other metals in soot, *e.g.*, copper, gallium, thallium, silver, chromium, lead, &c. Both nickel and cobalt occur in some varieties of commercial iron and steel; cobalt is especially likely to be present in traces in Bessemer or other steel in which spiegeleisen or other manganese alloy is used in the manufacture. A piece of a Sydney tram-rail, a horse-shoe picked up in the street, and nails from the same, all yielded traces of cobalt; nickel was not tested for, as the presence or absence of cobalt was regarded for the purposes of this inquiry as of more importance.

In spite of the presence of cobalt and nickel in some telluric irons, dusts, and soils, I still think that some, if not most, of the metallic iron (containing nickel and cobalt) found in dusts, such as have been described in this paper, is of meteoric or cosmic origin; the particles resemble those obtained from meteorites and do not look like pieces abraded from manufactured articles; further, they are not usually rusted to any great extent, whereas small particles of ordinary iron and steel (even if small amounts of cobalt and nickel are present) usually rust quickly; the difficulty is to prevent them passing wholly into the form of oxide; then too, the minute spheres of iron found in what are regarded as meteoric dusts and deposits are not found in flue dusts nor in volcanic dusts; as already pointed out, they have, however, been formed artificially by Prof. Schuster from meteorites.

The following shows, however, that a telluric form of spherulitic iron does occur:—In the *Transactions of the Royal Society of Canada* for 1890, Dr. G. C. Hoffmann describes an occurrence of metallic iron, containing nickel and cobalt, on St. Joseph Island, Lake Huron, Ontario. The iron occurs as minute spherules in a thin coating of limonite on the fissure faces of surface specimens of quartzite, the spherules amounting to 60 per cent of the coating by weight. The largest spherules are about 0·3 m.m. in diameter. Sp. gr. 6·86. The part of the spherules soluble in hydrochloric acid contained:—

Iron	97·79
Magnesia	0·57
Nickel	0·11
Cobalt	0·23
Copper	0·10
Sulphur	0·13
Phosphorus	1·07
	100·00

The portion insoluble in hydrochloric acid (non-metallic), 9·76 per cent, was made up of spherical and ovoid grains, and consisted mainly of silica. The spherules were made up of a siliceous nucleus, coated with a humus like substance, which in turn was covered with the metallic layer; the author suggests that this metallic layer was probably due to the reduction of an iron salt by organic matter.

The presence of a nucleus of silica or other non-metallic matter in the spherules, regarded as of cosmic origin, has not been recorded; further, the meteoric spherules show traces of fusion, hence I think the Canadian spherules are quite distinct.

Finally, although there appears to be no doubt whatever that there is a constant gentle rain of meteoric dust falling upon the earth's surface, and at times it is probably greater than at others, especially after the periodic meteor displays, the evidence certainly does not show that the dust storms, dust, haze, red rain, mud showers, &c., are due to any unusual descent of meteoric matter; hence it is a misnomer to call the deposits from such "meteoric dust."

Experiments on Plaster-of-Paris; the Setting of Plaster.—Ch. Cloëz.—When anhydrous plaster is thrown into a certain quantity of water, the temperature rises rapidly to 14—22° above the original temperature, then in about ten minutes it drops from 4° to 6°, and remains stationary for some time, and finally rises again, reaching a point higher than the one it first went to. This series of phenomena is absolutely independent of the amount of water used for mixing. Experiments were made, and the results are shown in curves, to determine the best proportion of water and plaster necessary to obtain sufficient hardness when the plaster was set. The setting of the plaster is proved to be due to the succession of the following three phenomena:—1, Hydration; 2, solution; 3, solidification of a supersaturated solution.—*Bull. Soc. Chim.*, Series 3, xxix., No. 4.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvi., No. 26, June 29, 1903.

Influence of Non-saturated Radicles on the Rotatory Power of Active Molecules. α-Allyl- or Propyl-δ-methyl-β-cyclopentanonecarbonic Ethers.—A. Haller and M. Desfontaines.—Unsuitable for abstraction.

Oxidation of Manganese Salts by Alkaline Persulphates in Acid Liquor.—H. Baubigny.—In neutral solution the oxidation of manganese salts by alkaline persulphates is stopped by the immediate formation of a brown colour, which is accentuated by the action of heat. In acid medium, on the contrary, the action takes place less violently, especially if slowly heated, and at first a pale rose colour appears like the ordinary colouration of permanganic acid. This disappears to give place to a brownish-black precipitate of oxide, the liquid above once more becoming slightly rose coloured. The author's researches were specially directed towards the action of $KMnO_4$ on an acid solution of $MnSO_4$.

New Plumbic Derivatives. Preparation; Thermochemical Investigation.—Albert Colson.—The decomposition of plumbic tetracetate by the fixed acids is comparable to the decomposition of ordinary salts, and allows of the preparation of plumbic derivatives, which do not have the ordinary action on minium nor the action with chlorine which ordinary lead salts possess. To prepare such salts it is necessary to operate in a vacuum and to keep the temperature low, otherwise reduction takes place and normal salts appear.

Organic Base containing Phosphorus. Its Constitution and Certain of its Salts.—P. Lemoult.—The reaction of PCl_5 on boiling aniline is often very violent, but can be employed to obtain a hitherto unknown derivative of pentabasic phosphoric acid, $P(OH)_5$. The reaction, however, does not take place according to theory, giving as it would $P{\equiv}(NHC_6H_5)_5$, but stops with the formation of a tetranilide compound, chlorophosphotetranilide, $PCl(NHC_6H_5)_4$, a substance already obtained by Gilpin. The reason of the apparent stopping of the reaction is due to the fact that this body is not an acid chloride, but the chlorohydrate of a new base, which the author now isolates, and obtains salts with HCl, H_2SO_4, HNO_3, and chloroplatinate. The base is trianilidophenylphosphimide, $(C_6H_5NH){\equiv}P{=}NC_6H_5$.

Volumetric Estimation of Nitric Acid.—M. Débourdeaux.—The author devises a method of estimation of nitric acid which does away with a number of the practical difficulties connected with the ordinary volumetric analysis of nitrates, and presents the following advantages:—(1) A liquid scarcely alterable by contact with air is used; (2) a sulphuric medium remains which renders titrations very easy; (3) the use of carbonic dioxide is avoided; (4) the estimation is very rapid; (5) the results obtained have an accuracy within 1/200th of the whole. The method is based on the action of nitric acid on oxalic acid. The proportion of oxalic acid destroyed is determined by an estimation with permanganate of potash.

Silicon Amide and Imide.—Em. Vigouroux and M. Hugot.—Silicon amide results from the action of ammonia on silicon chloride at a temperature lower than 0°. When the temperature rises above 0° the amide slowly loses ammonia gas, and a residue is left which is the imide, $Si(NH)_2$. At 120° the decomposition is complete. Both bodies are thus prepared in a state of purity, as can be shown by analysis.

Compounds of Hydroferrocyanic Acid with Organic Bodies.—MM. Chrètien and Guinchant.—Hydroferrocyanic acid forms with ether a compound containing 1 mol. of acid and 2 mols. of ether. This compound is only formed or destroyed under the influence of catalytic agents, such as water vapour. It can absorb up to 0·71 mol. of ether at 0°, giving a solid solution whose concentration varies with the temperature and with the tension of the vapour in the surrounding medium.

Preparation of Primary Alcohols by means of the Corresponding Acids.—L. Bouveault and G. Blanc.—The primary alcohols can be prepared by reducing an aldehyde, R—CHO, by means of sodium amalgam. The aldehyde is first produced by calcination with calcium formate from the calcium salt of the acid, $R{-}CO_2H$, or by another method a chloride or anhydride of the acid is reduced by sodium amalgam or a zinc copper couple. Both these methods give a poor yield of alcohol. The authors improve on these methods, and find that the methylic or ethylic ethers of the fatty acids are reduced by sodium in presence of absolute alcohol according to the equations:—

$$R{-}CO_2C_2H_5 + 2H_2R = R{-}CH_2OH + C_2H_6O.$$
$$R{-}CO_2C_2H_5 + Na_4 + 3C_2H_6O = R{-}CH_2OH + 4C_2H_5ONa.$$

MISCELLANEOUS.

British Association (Section B), 1903.—In his opening Address to the Section, the President, Prof. W. N. Hartley, F.R.S., proposes to give a brief account of twenty-five years' work in Spectroscopy applied to the investigation of the composition and constitution of terrestrial substances, both organic and inorganic, and to review the present position of spectroscopy chiefly in relation to chemical theories, indicating where it may be usefully and profitably extended. The following papers will be read:—

"Dynamic Isomerism," by T. M. Lowry, D.Sc.
"Hydroaromatic Compounds," by Dr. A. W. Crossley.
"The Cause of the Lustre produced on Mercerising Cotton," by J. Hübner and W. J. Pope, F.R.S.
"Mutirotation and the Glucoside Constitution of Glucose," by Dr. E. F. Armstrong.
"A Contribution to the Constitution of the Disaccharides," by T. Purdie, F.R.S., and J. C. Irvine, D.Sc.
"Some Derivatives of Fluorene," by Miss Ida Smedley.
"Fluorescence as Related to the Constitution of Organic Substances," by J. T. Hewitt, D.Sc.
"The Cholesterol Group," by Dr. R. H. Pickard.
"On Essential Oils," by Dr. O. Silberrad.
"Freezing-point Curves of Binary Compounds," by J. C. Philip, Ph.D.
"Action of Diastase on the Starch Granules of Raw and Malted Barley," by A. R. Ling.
"Action of Malt Diastase on Potato Starch Paste" (Part I.), by B. F. Davies, B.Sc., and A. R. Ling.
"Action of Malt Diastase on Potato Starch Paste" (Part II.), by A. R. Ling.
"Some Properties of Sodium Hydride," by A. Holt.
"On a Method of Separating Cobalt and Nickel and the Volumetric Determination of Cobalt," by R. L. Taylor.
"The Influence of Small Quantities of Water in bringing about Chemical Reaction between Salts," by E. P. Perman, D.Sc.
"Sur le Spectre du Silicium," and "Sur les Procédés de Photographie Spectrales applicables à la pratique des Laboratoires de Chimie," by M. le Comte Arnaud de Gramont.

Dr. W. A. Bone will open a discussion on the genera question of Combustion by a paper on the Combustion o Methane and Ethane.

Synthesis of Pyridinic Derivatives.—K. Bittner.—Quinolein dicarbonate of methyl, $C_5H_3N(CO_2CH_3)_2$, dissolved in acetate of methyl, and treated with sodium when heated to 80°, gives a salt of sodium which is precipitated by ether from its alcoholic solution. This salt crystallises in yellow needles, which become resinified immediately on contact with the air. It answers to one of the two following formulæ:—

$$C_5H_3N\begin{<}CO\\CO\end{>}>CNaCO_2CH_3 \text{ or } C_5H_3N\begin{<}CONa\\CO\end{>}>C-CO_2CH_3.$$

On the addition of hydrochloric acid we obtain yellow needles soluble in water; they consist of *pyridanedione-carbonate of methyl*, $C_{10}H_7NO_4$. The barium salt occurs in yellow needles. The *monoxime*, $C_{10}H_8O_4N_2$, is also in yellow needles, soluble in boiling water. *Anhydro-bis-pyridanedione*,—

$$C_5H_3\begin{<}CO\\CO\end{>}>C=C\begin{<}CH_2\\C_5H_3N\end{>}>CO,$$

is obtained by the action of heat at 100°, on the previous sodium salt, in acetic solution. It forms violet flakes insoluble in the usual solvents, but is soluble in concentrated acids giving a green solution, and in concentrated alkalis giving a blue solution.—*Berichte*, vol. xxxv., p. 1411.

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THE CHEMICAL NEWS.

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ON POLONIUM AND THE INDUCING CHARACTER OF RADIUM.

By F. GIESEL.

It has been found by Marckwald (*Berichte*, 1902, xxxv., 2285, 4239) that metallic bismuth, which is immersed for some time in a hydrochloric acid solution of Curie's bismuth polonium, acquires to a remarkable extent the property of emitting α-rays. Marckwald considers that the precipitate formed on the bismuth consists, at any rate in part, of metallic polonium, and regards the electrolytic separation as the proof of the existence of an (electro-negative) element differing from bismuth and allied to tellurium.

I (*Berichte*, 1902, xxxv., 3608) was successful in confirming Marckwald's observation with my purified polonium preparations, only no trace of a precipitate or a colouration was to be seen on the bismuth. As the non-appearance of a precipitate seemed to argue against Marckwald's theory, and in any case the prospect of obtaining sufficient quantity of the element in question was very remote, I tried to approach the question of the nature of polonium in a different manner.

In attacking this problem, I was guided by the opinion which I had previously expressed, that polonium may be bismuth acted upon inductively by radium, a view which was forced upon me by experience in direct experiments repeatedly performed when preparing preparations of polonium (*Berichte*, 1902, xxxv., 3610). As in my earlier experiments, less attention had been paid to α-radiation, and I had recently found (*Berichte*, 1903, xxxvi., 729) that this was developed both in metallic bismuth and also in platinum and palladium by the action of a solution of bismuth polonium chloride, it was important to investigate how a radium solution would behave. It may be safely asserted that the clean surface of the metals guaranteed the possibility of perfectly removing every trace of the *soluble* primarily active reagent, which cannot be vouched for in the case of precipitates even with the most careful washing. This appears all the more important when it is remembered that even one-half a millionth part of radium salt, present as an impurity, is sufficient to cause appreciable phosphorescence of the barium platinum cyanide screen.

In fact, it is now easily possible to impart to bismuth or the platinum metals, by *momentary* contact with radium, properties which exactly resemble those produced by polonium.

If a freshly cut piece of bismuth is placed in a solution of 0·01 grm. radium bromide in 1 c.c. water, after remaining there for one to two days, the bismuth shows strong α-radiation and no β-radiation.

Note.—The non-appearance of β-radiation, after keeping for two weeks, may perhaps be employed as a control experiment for demonstrating the absence of radium. For testing for α-rays the zinc sulphide screen was used, and for β-rays the barium platinum cyanide screen. All α-radiation produces on the zinc sulphide screen the scintillation described by Crookes, and observed by Elster and Geitel, while the β-radiation appears to produce only uniform illumination. The effect of a current of air on the scintillation can only be observed in the emanation of my emanation substance (*Berichte*, 1903, xxxvi., 342).

The greatest possible care was taken to remove every trace of radium salt from the bismuth,

Platinum-wire and palladium-foil, before being introduced into the radium solution, were rubbed with emery and sea-sand, washed with hydrochloric acid and distilled water, and ignited. After treating with the radium solution, like the bismuth, they were carefully washed with hydrochloric acid and distilled water to free them from the radium salt.

Bismuth is decidedly superior to the platinum metals in acquired activity, and seems to be best suited for accumulating the positive electrons of radium. It is noteworthy that the part of the platinum wire which was beyond the end immersed in the radium solution in the test-tube, and thus was only in contact with the air, also showed decided activity (α-radiation). The line of separation of solution and air was marked on the wire by a short zone of greatly diminished activity.

The α-radiation thus artificially communicated by the radium to the bismuth, palladium, and platinum shows no decrease, as far as has been observed. As it has hitherto always been found that the activity caused by induction diminishes with the time, comparatively speaking quickly, it is of great importance to investigate the limitations of this law by the manner and kind of induction, for which a longer time of observation is necessary.

The small quantities of bismuth and palladium passing into the hydrochloric acid solution in the above experiments were precipitated with sulphuretted hydrogen. The precipitates (especially the palladium sulphide), in spite of repeated washing, emit β-rays strongly. From what has already been said it could not be deduced whether this radiation is due to the adherence of radium; it can only be shown how it behaves with regard to the constancy of the activity.

I was able also to confirm the observation of the Curies, concerning the development of heat by radium, which can be proved in a very simple way.

If a thermometer is lowered into a glass flask containing 0·7 grm. radium bromide, in a short time it rises 5° above the temperature of the surroundings, and remains at this temperature as long as it is kept in the flask. When held over a capsule closed with a sheet of mica and containing 0·3 grm. radium bromide, the thermometer showed an increase of temperature of almost 2°, if it was protected from currents of air.—*Berichte d. Deutsch. Chem. Gesell.*, 1903, xxxvi., 2368.

THE ACTION OF MERCUROUS NITRATE AND OF THE NEUTRAL MERCUROSO-MERCURIC REAGENT ON ANTIPYRINE.

By A. MOULIN.

In a previous paper, in February, 1901, we described the action of the neutral mercuroso-mercuric reagent, as prepared by M. Causse (*Bull. Soc. Chim.*, vol. xxiii., p. 493), on asparagin, dulcin, and saccharin.

This reagent reacts easily on these compounds, giving substitution compounds by the fixation of mercury on the amidised group.

With dulcin, if we work with hot solutions, the reaction is more complex; there is a decomposition of the molecule, and the formation of cyanate of mercury, and of a violet colouring matter described by Kingel. The reaction, which is easy to obtain, was described in our inaugural thesis (Lyon, January, 1902). The action of this reagent on antipyrine is much more complex, and gives rise to the formation of interesting nitro and nitroso-compounds.

I.—*Action of Mercuroso-nitrate on Antipyrine.*

If we dissolve antipyrine in a saturated solution of nitrate of potassium, and add a solution of mercurous nitrate dissolved in water saturated with nitrate of potassium, an abundant precipitate is formed immediately, having a greyish appearance, and consisting of beautiful colourless needles. The grey appearance is due to the presence of numerous globules of mercury.

The precipitate thus obtained is taken up with boiling alcohol at 60°. On cooling, small white crystals are deposited, slightly soluble in water; soluble in alcohol, especially when heated; soluble in nitric acid, even when

very dilute. Soda and ammonia also dissolve them. They are soluble in sulphuric acid, giving a red solution; they answer to the formula $C_{11}H_{12}N_2O(NO_3)_2Hg$.

Analysis gives the following figures :—

	Found.	Theory.
C	24·58 and 24·96	25·78
N	9·98 ,, 10·13	10·93
Hg	38·68 ,, 38·47	39·06

II.—*Action of the Neutral Mercuroso-mercuric Reagent on Antipyrine.*

This reagent is obtained easily in the following manner. 50 c.c. of mercury and 1 litre of a mixture of equal parts of water and concentrated nitric acid are placed in a flask. After the complete solution of the mercury, a current of air is passed through to remove the nitrous fumes; the flask is then left to stand in a dark place until the contents are completely decolourised. Measure off 100 c.c. of this reagent, and add 400 c.c. of a saturated solution of nitrate of potassium; heat on the water-bath, and add some yellow oxide of mercury until saturated; allow to cool and filter.

If we add this reagent very gradually to a solution of antipyrine, we soon notice the formation of a white gelatinous precipitate, which is at first dissolved on stirring and afterwards permeates the entire liquid, which becomes green. The flask in which the reaction has been effected is then placed on the boiling water-bath. The precipitate becomes crystalline, and takes a reddish tinge, with a tendency towards yellow. Allow to cool, and collect the precipitate, which is washed and dried over sulphuric acid. The product thus obtained has not a constant composition, it is formed of a mixture, and it is necessary to purify it.

For this purpose, the crystalline powder obtained is treated with concentrated nitric acid until this acid no longer takes a brown colour. A bright red powder remains, slightly soluble in water, which it colours a reddish yellow; it is slightly soluble in nitric acid; sulphuric acid appears to dissolve, but in reality decomposes it. Ammonia transforms it into a brownish yellow compound. The compound thus obtained answers to the formula $C_{11}H_{12}N_2O(NO_2)_2Hg_2$.

Analysis gave the following results :—

	Found.	Theory.
C	19·96 and 20·01	19·41
N	8·31 ,, 8·40	8·23
Hg	59·18 ,, 58·10	58·82

The nitric acid used for the washing of this body is coloured strongly brown. It is diluted with a large quantity of water, when a precipitate is formed immediately. It is left for twenty-four hours, and the precipitate is collected on a filter, washed with distilled water, and dried over sulphuric acid.

It occurs in the form of a crystalline powder, of a chamois yellow colour; it is soluble in nitric acid, and partially so in sulphuric acid; it is very slightly soluble in water, and answers to the formula $C_{11}H_{12}N_2O(NO_2)_2Hg$.

Analysis gave the following results :—

	Found.	Theory.
C	26·30 and 26·91	27·50
N	10·73 ,, 11·31	11·66
Hg	40·01 ,, 41·06	41·66

These two compounds explode when heated to 205—210°, they decompose with violence, leaving a voluminous carbonaceous residue, and give off a gaseous product having a strong odour of garlic; at the same time they deposit a yellowish powder which we have not yet examined.

The mother liquors resulting from the preceding operations are evaporated on the water-bath, then on the sand-bath, but the temperature must not rise above 140°; the residue, after washing with distilled water, appears as a reddish-yellow powder with a crystalline texture, and is no other than the compound $C_{11}H_{12}NO_2(NO_3)_2Hg$, previously described and obtained by quite a different method. The colouration in this case is due to traces of nitroso compounds, which we have not been able to remove entirely.

Conclusions.

Mercurous nitrate reacts easily on antipyrine in solution, giving a nitro-mercurate of antipyrine, answering to the formula $C_{11}H_{12}N_2O(NO_3)_2Hg$.

The action of the neutral mercuroso-mercuric reagent is much more complex. There is first the formation of the preceding compound, and at the same time the formation of nitroso-mercurous antipyrine and nitroso-mercuric antipyrine, which are easily distinguished by their colour and their solubility in nitric acid, decomposing with explosive force at about 205°, and answering to the formulæ $C_{11}H_{12}N_2O(NO_2)_2Hg_2$ and $C_{11}H_{12}N_2O(NO_2)_2Hg$.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 5.

NOTE ON THE

ELECTRO-METALLURGY OF ALUMINIUM.*

By GUSTAVE GIN.

Choice of the Electrolyte.

In solution, in a fused salt, the compounds of aluminium can be electrolysed with the mono- or bivalent metalloids.

The electrolysis of the double salts may be compared with that of the binary compounds in this sense, that there is a primary decomposition of the complex molecule, then dissociation of the binary constituent, which is the least exothermic under the conditions of the experiment.

The electrolytic bath, comprising the electrolyte (properly so-called) and its solvent, ought to satisfy the following physical conditions:†—The fusing-point must be high; when fused, the electrolyte must be of suitable fluidity, and of a density lower than that of melted aluminium; it should have very little vapour-tension and an electric resistance as low as possible.

From the chemical point of view, the compound to be electrolysed should be chosen from among the least exothermic. This condition is not so rigid as the preceding ones, but it corresponds to the minimum expenditure of energy, and it is as well to appreciate its importance.

Now, for any particular electrolyte, as the weight of the aluminium set free depends only on the amount of electricity used, it results that *the energy used is exactly proportional to the tension of the bath.* Now this tension is divided into two parts, of which one is a function of the resistance of the bath, the distance apart of the electrodes, and the strength of the current. The other portion—that is to say, the tension of polarisation—corresponds to the passage of the ions to the molecular state, and it depends on the heat of formation of the electrolyte, which comprises the heat of the ionisation of the constituents.

Our knowledge of the properties of fused salts is much less complete than that of aqueous solutions, and is quite insufficient to enable us to solve all the difficulties of calculating the tension of polarisation.

However, we may presume that, in igneous solutions of the haloid salts of aluminium, dissociation is almost complete, and this presumption appears to be verified in the electrolysis of fluoride of aluminium, concerning which Minet has collected observations of great exactitude.

If the ionisation is complete, the heat corresponding to the tension of polarisation is equal to the sum of the heats of ionisation of the anion and of the cation, and we shall have—

$$Q = J_F + J_{Al\,\frac{1}{3}} = 50750 + 40100 = 90850 \text{ c. gr. d.},$$

* A Paper read at the Fifth International Chemical Congress at Berlin, 1903 (Section X.).

† These conditions were formulated by Minet at a time when electrochemical research was very much more difficult than it is to-day.

which corresponds to a tension of—

$$E = \frac{90850}{23067} = 3{\cdot}93 \text{ volts.}$$

As a matter of fact, Minet found only 2·5 volts experimentally, but the disagreement is only apparent, and is caused by not taking into account the secondary reactions produced by the liberated fluorine in the above calculation.

In a communication to the Congrès de Metallurgie de 1900, M. Heroult admitted that in the electrolysis of cryolite no fluorine is given off, and that an acid fluoride of sodium is formed, soluble in water; that is to say, that in the decomposition of Al_2F_6, the 6NaF would correspond to the formation of 6 molecules of the compound NaF_2. Now, as the mono-atomic elements are only able to form one single series of compounds among themselves, the body NaF_2 cannot exist, and it is probable that the soluble body observed was simply fluoride of sodium forming the residue of the decomposed cryolite.

It is quite true that fluorine is not given off in the free state, but in the form of a tetrafluoride of carbon mixed with a more highly carburetted fluoride.

Further, this reaction has the greatest analogy with that which accompanies the electrolysis of alumina in solution, which gives carbonic acid mixed with carbonic oxide at the anode.

Now, if we take into consideration the reaction of the fluorine on the anode, the preceding formula must be written—

$$Q = J_F + J_{Al}\tfrac{1}{3} - \text{the heat of formation, } C\tfrac{1}{4}F,$$

or—

$$Q = 50750 + 40100 - 33400 = 57450,$$

from which we get—

$$E = \frac{57450}{23067} = 2{\cdot}49 \text{ volts,}$$

a figure which coincides with that found by Minet.

Electrolysis of Al_2O_3.

Let us pass now to the electrolyte of Heroult and Hall, in which it is oxide of aluminium that is decomposed. We shall have—

$$Q = J_O\tfrac{1}{2} + J_{Al}\tfrac{1}{3} - \text{the heat of formation, } C\tfrac{1}{4}O,$$
$$= 34950 + 40100 - 24400 = 50650 \text{ c. gr. d.,}$$

from whence we get—

$$E = \frac{50650}{23067} = 2{\cdot}19 \text{ volts.}$$

In applying the method of Max Le Blanc for the measurement of the tension of polarisation of a fused bath containing $Al_2O_3 + (Al_2F_6.6NaF)$, I found 2·3 volts as the mean of four observations.

Electrolysis of Al_2S_3.

For sulphide of aluminium we have—

$$Q = J_S\tfrac{1}{2} + J_{Al}\tfrac{1}{3} - \text{the heat of formation, } C\tfrac{1}{4}S\tfrac{1}{2}.$$

But the heat of formation furnished by the tables corresponds to S in the solid state, while the compound CS_2 is formed from S in the gaseous state. We get a closer figure to the heat of formation by adding to the number in the table the heat of volatilisation calculated by de Forcrand's formula; that is, 21600 c. gr. d. for T = 720° C.

Under these conditions, the heat of formation of $C\frac{1}{4}S$, instead of being negative, becomes positive, and passes from −6,450 to +4350.

Therefore we get—

$$Q = -6300 + 40100 - 4350 = 29350 \text{ c. gr. d.,}$$

from whence we have—

$$E = \frac{29350}{23067} = 1{\cdot}27 \text{ volts.}$$

From the above figures we calculate that, for the preparation of 1 kilogrm. of aluminium by means of the electrolytes dealt with, the energy consumed will be given approximately by one of the following formulæ, in which K_F, K_O, and K_S are quantities varying between 16 and 19 kilowatts:—

For Al_2F_6.. .. .. $T = (K_F + 8{\cdot}5)$ K.W.H.
Al_2O_3.. .. .. $T = (K_O + 7{\cdot}5)$,,
Al_2S_3.. .. .. $T = (K_S + 4{\cdot}4)$,,

The maximum difference between the various electrolytes is thus probably about five kilowatt-hours. At the present price of electric energy furnished by large water-falls, this difference represents only a few centimes per kilogrm. of aluminium.

Thus we find that the cost of the aluminium depends much less on the more or less easy decomposition of the electrolyte than on the cost of that electrolyte. The economic problem is therefore of a chemical rather than an electro-chemical order.

I have one more interesting remark to make before finishing:—In electrolysing a mixture of artificial cryolite and sulphide of aluminium, and stopping the operation before its completion, I observed the presence of a subsulphide of aluminium in the electrolyte; it was distinctly crystalline, and of a bright cinnabar-red colour. I am following up the examination of this compound, the existence of which could be foreseen from the work of M. Sabatier.

CHLORINE SMELTING, WITH ELECTROLYSIS.*

By JAMES SWINBURNE.

Argument.

Chlorine smelting, a new process covering wide domain in metallurgy. Present processes, furnace reductions. Costly and give impure metals. Can only treat certain ores. Chlorine process treats pure sulphides, and gives still better results on mixed or refractory sulphides. Process is in three stages; writing Zn for Zinc, and M and N for other metals: —I. $ZnS + MS + NS + 3Cl_2 = ZnCl_2 + MCl_2 + NCl_2 + 3S$. II. $ZnCl_2 + MCl_2 + NCl_2 + 2Zn = 3ZnCl_2 + M + N$. III. $3ZnCl_2$ electrolysed $= 3Zn + 3Cl_2$. More detailed description. Working cost of process. Capital cost. Antimony. Arsenic. Bismuth. Cobalt. Copper. Gold. Iron. Manganese. Nickel. Silver. Tin. Zinc. Rule for capital.

Present Processes.

It will seem rather late in the history of metallurgy to bring forward a scheme which aims at nothing less than a complete revolution of the major part of the art of metallurgy, but this is a new Society, and it is but fitting that a new process be brought before it for discussion and probably criticism, but I hope for and expect help in the way of suggestions and information from many of the members who are especially qualified to give it.

At present we may take it the normal process for obtaining a metal is to convert it into oxide and reduce the oxide by carbon. Iron is a good example. It occurs as oxide, and is reduced by carbon or its monoxide. The result of this process is a metal which is very cheap, but very impure. The economical value of pure iron is unknown. It may be very high. More will be said about that presently.

Zinc is obtained purely by reduction, though work has been done on its extraction by electrolysis, especially from aqueous solutions. The bulk of the zinc of the world is obtained by a very crude method of reduction by carbon. Copper involves a furnace reduction process which may be partly classed as carbon reduction, and partly as a direct action analogous to the alternating reduction of lead sulphide. Tin is reduced by carbon. Electrolysis has come to the front, however, in the reduction of sodium and aluminium.

The great drawback to the carbon reduction processes is

* A Paper read before the Faraday Society, June 30, 1903.

that the metals so obtained are always impure, the refining often being exceedingly expensive; there is a great deal of waste, and many mixed, or so-called refractory ores, cannot be treated at all.

Electrolysis provides an admirable means of getting many of the metals down, but the difficulty is generally in getting the metal from the ore to a suitable condition for electrolysis. Thus copper is very easily deposited from, say, copper sulphate solution, but it is by no means easy to prepare a copper sulphate solution economically from a copper ore.

There is also difficulty as to the anodes. Carbon is corroded, and lead or antimonial lead need a still higher electromotive force. Aqueous solutions of lead salts cannot e made economically from lead ores, and their electrolysis gives rise to lead sponge, which cannot be dealt with. Zinc gives similar troubles.

What is wanted to displace furnace reduction of oxides and sulphides is to convert the ores into salts of the metals that can be easily and cheaply electrolysed, and to do this simply, efficiently, and economically.

The Chlorine Process.

The process I have the honour to bring before the Society is simplicity itself. The sulphide ore is treated with chlorine so as to displace the sulphur and absorb all the chlorine. The chloride is then electrolysed to get the metal and recover the chlorine. This is the process in its naked simplicity. When all the details necessary, even in connection with complex ores, are considered, in comparison with existing methods, the process is exceedingly simple.

As a good example, suppose pure galena is to be smelted. The galena is treated with hot chlorine, so as to form lead chloride and sulphur. The sulphur is condensed as brimstone, and the lead chloride is electrolysed in the fused state, producing lead and chlorine. If there is silver or gold present, the fused chloride of lead is treated with metallic lead. This replaces any gold or silver there may be, and the precious metals alloy with the remaining lead, so that ultimately a bullion is produced as rich as may be desired, the only limit being its melting-point, which must not be too high. The cost of de-silverising by the ordinary processes is thus saved. This process thus recovers all the lead, all the silver and gold, and nearly all the sulphur. If the electrolyte vats were so tight that no air got in, all the sulphur would be saved, but in practice a little sulphur is always burned into SO_2.

Pure or nearly pure lead sulphide is easy to smelt in the ordinary way; but this smelting does not separate the silver, and is thus incomplete. In time, therefore, the chlorine process is likely to replace the present methods, even for pure ores.

Take another example, pure zinc sulphide; the process is exactly analogous to that for pure galena. But in practice zinc blende contains gangue and generally iron, and these must be separated.

One of the great advantages of the chlorine process is that it is applicable to mixed ores, which are often absolutely refractory and useless otherwise. This process makes concentration quite unnecessary, unless merely for eliminating gangue, as the presence of several metals gives rise to no difficulty. In no case has one metal to be lost in order to extract another; and in no case is a metal brought out impure or needing refining.

Take, for example, a mixture of sulphides of lead, zinc, and iron, with some silver. An immense amount of work has been done on this class of ore, and great progress has been made in concentrating, so that one part will leave enough zinc to be worked, and little enough lead not to interfere with the metallurgy, and the other part will leave enough lead and little enough zinc. Each portion is smelted for one metal only, the other being worse than wasted, as it is a nuisance. An intermediate ore, often a large proportion, is thrown away.

The new process takes the ore just as it comes from the mine, without any previous treatment; or, better still, it takes the slimes, such as the Broken Hill slimes, which are at present accumulating as a monumental memorial to the barbarity of presenting smelting processes. The slimes contain zinc, lead, iron, silver, and gangue. Hot treatment with chlorine converts the whole of the metals into chlorides, producing a broth of mixed fused chlorides and gangue. The silver is extracted by substitution of lead, the lead is extracted by substitution of zinc, and the iron is thrown out as ferric oxide, not as metal, zinc oxide being used as substitute, and the gangue is got out by filtration. We have then nothing left but zinc chloride, and this is electrolysed to yield zinc and chlorine.

The process thus consists of three essential elements:—

Treating the ores with chlorine.
Chemical treatment of the mixed chlorides, by substitution, so that all the chlorine is combined with zinc.
Electrolysis of the zinc chloride to extract the zinc and recover the chlorine.

One of the chief merits of the process is that it is so perfectly cyclical. The chlorine merely goes round and round; the works takes in ore and electrical energy, and turns out metals, sulphur, and gangue. In treating sulphide ores with chlorine, as in analysis, or in the action of chlorine on sulphides generally, chloride of the metals and chloride of sulphur are produced. This is the reaction described in most text-books of chemistry. The formation of chloride of sulphur would be fatal to the process, however, as we should lose both the chlorine and the sulphur, and there is no convenient way of getting rid of large quantities of this offensive compound, far less of recovering the chlorine and sulphur. Decomposing with water is not a cyclic or a practical process.

The discovery that sulphide ores can be decomposed on the large scale by chlorine so as to give off sulphur and not its chloride, is, if we may say it with modesty, a possible turning-point affecting a vast realm of metallurgy.

The middle parts of the process, by which the mixed chlorides are converted into chloride of zinc by substitution and elimination of the other metals and of the gangue, involve ordinary chemical engineering only, though there is considerable room for ingenuity in inventing and working out the methods on a large scale.

The electrolysis of zinc chloride is supposed to be very difficult or impossible. We have overcome any difficulties. Zinc is chosen as the final metal to be separated from the chlorine for two reasons: because it is chemically easy to substitute it for all the metals we want to extract, as it is very electro-positive; and because it is easy to extract by electrolysis.

Smelting Lead Zinc Bluestone.

The actual process, as applied to some particular ore, may now be described. The Broken Hill slimes may be taken as a good example.

The crushed ore is run into a transformer. This looks like a small blast-furnace made of fire-clay with iron outside, or of lined iron. It runs continuously, and we may start our description at the stage when a tapping has just taken place. The transformer then contains about a hundredweight of fused chlorides and gangue. The gangue almost floats in the chlorides. If much lead is present much of the gangue floats, so there is no caking or silting up. The top of the transformer has a cone like a little blast-furnace. Ore is poured into the fused chlorides, and at the same time chlorine is blown in. The chlorine enters at the bottom by a sort of tuyere, which is a carbon tube. The cold part of this tube is connected to an iron pipe, which brings the chlorine. Dry cold chlorine is easy to handle. It does not touch metals, and iron can be used freely. The chlorine bubbling through the fused bath displaces the sulphur, which comes off and is condensed. The action of chlorine on the sulphides in question evolves a great deal of heat, so that the transformer is self-heating, and there is no coal or coke firing or outside heating of any sort. The temperature is controlled by the rate of

admission of chlorine. If the temperature is too low chloride of sulphur may be formed. This may also be formed if there is a deficiency of ore supply. On the other hand, if the chlorine and ore are supplied too quickly, the transformer will get too hot, and some of the chlorides will distil over and be condensed with the sulphur. By running the transformer fast the temperature can be got so high that all the chlorides distil over, leaving only the gangue. The bulk of the transformer gives easy regulation.

The temperature is the main consideration in determining the size of the transformer. It must be of such a size that when running at its normal rate the heat is conducted through the lining and radiated from the surface at such a rate that the contents keep at the right temperature. There is considerable margin allowable in temperature, and the temperature is under control by regulating the flow of chlorine and of ore. The temperature can always be lowered by running in a little extra ore or reducing the chlorine ; but the chlorine feed depends on the electrolytic vats, and is practically constant. The larger the transformer the longer it will preserve its temperature with any fluctuations of chlorine supply, and the cheaper the pumping, labour, &c. It is therefore best to have large transformers. We have so far used a ten-ton, but a larger size with thinner lining will probably be better.

The amount of gangue in the ore is important. As the gangue is about the same density as the chlorides, a large amount may be present without inconvenience as to fluidity. If is of course an advantage to be able to work on ores with little metallic content. It is quite easy to work with the metallic contents only half the ore, or even less. Poorer ores can be made workable by addition of those with more metal. The temperature depends on the metals in the ore too. Thus blende heats much more than copper sulphide ; so that, other things being equal, a copper ore with little zinc should be run through faster, or mixed with, say, a zinc-lead ore.

To return to the working of the transformer, it is started with the remains of the last charge, and then chlorine and ore supplied till it is full. The regulation needs no skill. A hole can be opened at the top of the transformer, and as it is connected through the sulphur chamber to a chimney there is a general suction. This draws air in at the hole, which burns the sulphur vapour. The blue flame shows there is enough ore. If too little is fed, fumes of ferric chloride fill the top of the transformer and pass into the sulphur. This is to be carefully avoided, and there should be excess of sulphides in the transformer until the end of the charge. At the end the ore feed is stopped, and the transformer run till brown fumes appear. These are by-passed round the sulphur chamber. The charge is then run out, and allowed to cool.

At first great difficulty was expected in pumping the chlorine, as a pressure of some ten to fifteen pounds on the inch is needed when the transformer is nearly full. The pumping presents no difficulty, and a chlorine pump will run day and night continuously without trouble. The well-known patented method with sulphuric acid flooded pumps would have been available ; but such complications are quite unnecessary with dry chlorine. The dryness is of vital importance here.

We now come to the intermediate or chemical stage of the process. This varies with the ore used. We may take the Broken Hill slimes, and imagine there is copper too. This would be about as troublesome an ore as we could have. We have used the Broken Hill ore and mixed it with a Tasmanian copper ore, but we have chiefly worked on it alone. The fused mass from the transformer consists of chlorides of lead, zinc, iron, manganese, copper, silver, and gangue. It is run into water and through a filter-press when cool enough. This takes out the gangue and lead chloride, carrying most of the silver. The gangue is easily separated from the lead and silver chlorides, and these chlorides are then dried and fused in contact with lead, which extracts the silver and any gold ; and then with zinc, which gives lead, practically pure, and anhydrous neutral zinc chloride, which is ready for the electrolysis vats.

The filtrate from the press contains a little lead and silver in solution, and copper, iron, manganese, and zinc. The lead and silver are taken out with spongy copper. The copper is taken out as sponge or "cement" by zinc, and we have left iron, manganese, and zinc chlorides.

The iron is chlorinated up to the ferric state, and zinc oxide is added to cause precipitation. This throws down hydrated ferric oxide. This is the base of iron paint, and is marketable, its value depending on the colour obtained. The solution is further chlorinised in presence of more zinc oxide, and the manganese goes down as peroxide.

We have now substituted zinc for all the other metals in their chlorides, and have nothing left but zinc chloride. This is evaporated down carefully and fused. This decomposes some of the chloride, and makes an oxychloride. Steinhart evaporates *in vacuo* to produce neutral anhydrous zinc chloride. We have not done this ; we find that with cautious boiling down there is not much oxygen in the final result. This is got rid of in open preliminary vats, which use inexpensive anodes, which are gradually used up. The consumption is less than if all the oxygen went off as monoxide. The anhydrous neutral chloride from these vats is then added to that from the lead chloride substitution, and is taken to the final electrolysis vats.

The electrolysis vats are internally heated, as in the case of aluminium. The cathode is fused zinc, and the anode is carbon. Some makes of carbon do not stand well, but suitable carbons serve to stand permanently. Of course chlorine has no action on the carbons. The vats are kept under a very light suction, so that if there are any leaks air goes in instead of chlorine coming out. The carbons are not hot enough to be burnt by this small admission of air. As the vats are kept warm by the excess of the electrical power over the chemical, the larger the cell the lower the electromotive force, so that if the cell were large enough we could get down nearly to the electromotive force corresponding to the heat of formation of zinc chloride at that temperature. So far 3000 ampères has been the current used, but this means a very small vat. The output of fused salt vats is enormous in comparison with aqueous work. A 10,000 vat is now being tried. Above that size the current will be inconvenient. With the small vats four volts per cell is needed, with 10,000 ampères three should do. It is best to count on four ; this allowance ought to cover the power for the preliminary electrolysis too. The current efficiency is practically unity. Zinc smoke is of course formed if the temperature is too high.

The vats are very simple ; merely iron cases lined with fire-brick. The chloride soaks into the porous brick and solidifies somewhere, so it is really a vat with zinc chloride walls.

Cost of Process.

As to costs of the process ; the first thing to realise is that it smelts for all the metallic contents of the ore, not for only one. That all the metals are completely extracted. There is no waste by fumes or imperfect extraction, and there is no slag. The gangue looks like river sand. There is no room for loss. All that comes into the works is ore and electrical energy ; all that goes out is pig-metal, sulphur, gangue, and oxides. The chlorine goes round and round. There is no room for appreciable waste of chlorine either. A leak that would show in the balance sheet would make the works uninhabitable. There is, however, a trace of chlorine in the iron oxide, as it is apt to contain a little oxychloride. There is also a loss in collecting the hydrochloric acid from the boiling down of the zinc chloride. A little chlorine must therefore be added to the stock. This can be done by buying crude zinc chloride, or galvanising pickle, or precipitating calcium chloride with zinc sulphate. In out of the way places it is much simplest to buy zinc chloride, as it is more portable than hydrochloric acid.

It may be said that a process for such a problem must

be a maze of chemical operations, and when you come to the end you have to begin again. This is not the case here at all. The process has only three simple stages :—(1) Transforming sulphides into metallic chlorides and sulphur ; (2) substituting zinc for all the other metals in the metallic chlorides ; (3) electrolysing out the zinc, and recovering the chlorine.

Compare this with ordinary metallurgy. To describe the metallurgy of a single metal at all adequately requires a book. Try and explain even most superficially the metallurgy and refining of argentiferous lead, zinc, and copper to any one quite new to the subject in the few pages here devoted to description, and it will be seen how simple the new process is. Add to the description of the metallurgy of these metals an account of the refining of copper and zinc, and refining and de-silverisation of lead, and even then you have only half done. To make the comparisons on all fours you must give an account of the concentration and separation of refractory ores, and give a description of methods for dealing with a mixed ore of lead, zinc, silver, iron, and copper. There can be no doubt that though the steps in the new process sound unfamiliar to ordinarily trained metallurgists, it is in comparison ludicrously simple. But there is even more than this ; the new process treats ores, whose smelting by ordinary processes cannot be described, even with unlimited complications, because they are at present untreatable.

As to costs, everything depends on what ore is used, and where it is used.

The most obvious course is to work on refractory ores which are otherwise valueless, but leave large metal contents. The cost of the ore delivered at the works is then known. Thus even in England Blue-stone ore can be bought and delivered at from £2 10s. to £3 a ton, ready for running into the transformer. The metal content is £8 16s., taking zinc at £20, lead at £12, and silver at 2s. If higher prices can be maintained for pure metals, of course the content must be taken at a higher value. This figure includes all valuable contents.

The cost of the intermediate process is difficult to state, as it is a question of locality and labour. The capital in this part of the process is small, but in the estimates heavy allowance has been made for deterioration, and all other contingencies. On the other hand, the conversion, which alone is a new sort of chemical experience, is extremely simple and easy. The intermediate processes depend on the ore. Thus, if there is no copper, part is cut out altogether. If there is no iron, by which I mean not even enough to hurt the zinc, the transformer product would not be dealt with in the wet way at all. The wet way is to get rid of iron and manganese, and to get out copper. Lead and silver can be got out by substitution in the fused state with great ease, but copper has too high a melting-point, and is therefore taken out by the wet process.

To make a very safe shot, the cost of all the process except the energy for electrolysis may be taken at a rough figure of 30s. per ton of ore. This will easily cover all depreciation, a small percentage on capital, all labour and management. As the process uses ores with about half the contents metallic, though it can work with half sulphides, this means about 30s. per ton of chloride of zinc handled. Most of this work is pure circulation, agitation, and filtration, all cheap processes. The solution is not bulky, as it is used as strong as the filter-press cloths will stand. Evaporating down and preliminary electrolysis are the most expensive parts of the process, and they are not serious. The loss of chlorine, which has not yet been determined, may be taken as costing about 1s. a ton of ore for every 1 per cent of chlorine wasted, if it is made up by buying chloride of zinc. If it is made up by hydrochloric acid or calcium chloride, which is far cheaper where there is no carriage difficulty, the cost is about half that of zinc chloride. This loss of chlorine is included in the 30s. a ton of ore, and in the estimates to follow, as power is taken at prices in England where it is not cheap, we may assume we can get calcium chloride cheap. This does not complicate the estimate by showing a zinc output a little higher than the intake in the ore.

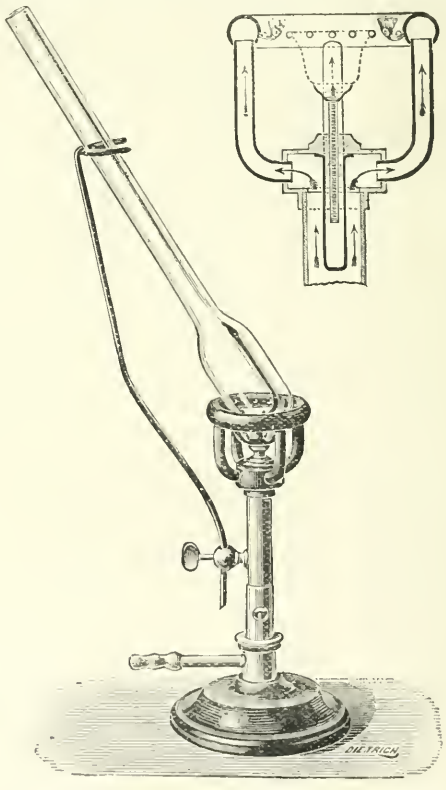
The cost of energy is very easily determined. If it is generated by steam-engines of high grade in this country in a convenient district, it may be taken as 0·25 per kilowatt-hour, including depreciation, coal, oil, repairs, labour, and management, and a small interest on capital. This is a close estimate, but one which can be realised on large plants running day and night on uniform full loads. The cost by producer gas and gas-engines is somewhat uncertain ; it may be taken at 0·125, though that is probably a very tight figure. Water-power in a favourable situation may be taken at 0·085. This refers to water-powers such as on the way down from the American lakes to the sea. It is for a works planted close to the generators, and does not cover rotary transformers, or step-down plant.

(To be continued).

A NEW GAS-BURNER.

By L. QUENNESSEN.

In the present method adopted for the assay of gold, silver, and platinum, after having cupelled to get rid of the oxidisable metals, the cornets are attacked with boiling nitric or sulphuric acids, and we meet with several difficulties during the operations in which the liquids are heated over Bunsen burners modified by Debray.



1. In the assay of gold and silver we boil the cornet first with nitric acid of 1·18 density, then, after decantation, with acid of 1·286 density.

In this operation the boiling does not go well ; to regulate it we are obliged to put a fragment of porous charcoal into the matras, obtained by calcining vetch seeds in a closed vessel.

Then, when the gold is present in very small quantities compared with the silver, especially when the alloy contains less than 200-thousandths of gold, the latter becomes divided into a very fine powder as the silver gradually dissolves, and by attaching itself to the sides of the vessel causes bumping, which may lead to losses by projection.

2. In assays of platinum and gold, in which it is necessary to dissolve the inquartation silver in concentrated boiling sulphuric acid, bumping also occurs on boiling the liquid, and this frequently leads to the breaking of the matras.

The new burner (which is shown in the accompanying illustration) obviates these drawbacks. The gas comes out through holes arranged round the interior of a crown, so that the heating is annular and the boiling is effected, no longer at the bottom, but round the sides of the matras. Thus projections are prevented. Further, according to the use for which this burner is intended, it is necessary that the heat can be applied at various heights. To effect this, the bottom of the matras is held by a copper support in the form of a tulip; this latter is braized to the upper part of a screw that can be turned up or down the axis of the heating crown; the end of this screw fits into a tube to prevent all loss of gas.

In assays of gold, it is no longer necessary to use grains of carbon, the use of which was often very inconvenient.

In assays of platinum, the parting with sulphuric acid, which can be boiled in from five to seven minutes, is effected with the greatest ease.

This burner can be used also in the estimation of nitrogen by Kjeldahl's process; this process is, in fact, much easier to carry out in assay matrasses on account of the length of their necks, which is much greater than that of the necks of flasks, even of the same capacity, generally used in chemical work.

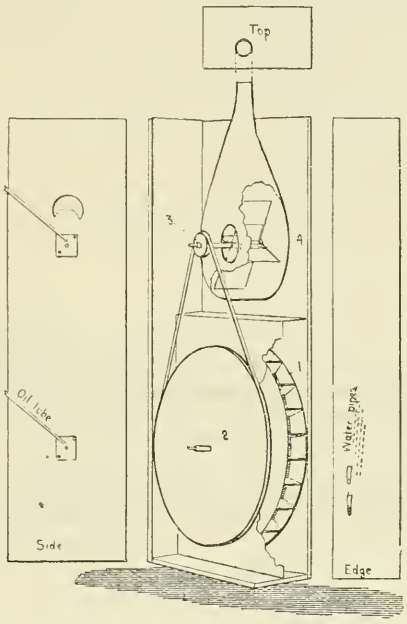
A CHEAP AND EFFICIENT WATER-BLAST.

By FRANK L. HANN.

The work performed in the chemical laboratory of Cornell College emphasised the necessity of a water-blast, and some of the well-known kinds were purchased. The laboratory is situated on the third floor of the building, where the water-pressure was found to be scarcely 30 pounds to the square inch. This was insufficient to maintain the blasts satisfactorily. It was therefore necessary to set about to devise a blast which would be suitable where the water-pressure is low, and which would give good results with a small jet of water. The apparatus here described has been in use for six months, and seems fully to meet the conditions.

Experiments with various devices were made, but the one that has given the most satisfactory results consists of a small water-wheel (1), a large pulley-wheel (2), connected by belt with a small one (3) for driving a fan-wheel (4), all of which are enclosed in a rectangular wooden box, 7 × 12 × 24 inches.

The water-wheel is 9·5 inches in diameter and 1·5 inches thick, and is made of galvanised iron. Its construction is something on the plan of an undershot wheel. There are twelve paddles on the rim, projecting an inch, against which the water strikes to produce the motion. Each paddle is placed in line with a radius of the wheel. The larger pulley-wheel has a diameter of 10 inches, is of a good quality of white pine, and was soaked for three hours in melted paraffin to prevent warping. It has a groove $\frac{3}{8}$-inch in diameter for the belt. These wheels are mounted on a $\frac{3}{8}$-inch shaft, turned down at each extremity to $\frac{1}{4}$-inch bearing. The smaller pulley-wheel is of wood, $\frac{3}{4}$ of an inch in diameter, with flanges $\frac{1}{4}$ of an inch deep. The fan-wheel consists of four wooden paddles and is 6 inches in diameter. This wheel and the smaller pulley are mounted on a $\frac{3}{8}$-inch shaft, which is likewise turned down to $\frac{1}{8}$-inch journals. The boxings in which the journals run are simply pieces of iron, $\frac{1}{8}$ of an inch in thickness, with holes drilled to fit the journals, and the iron pieces are fastened to the inside of the case. The water-wheel is separated from the rest of the apparatus by an air-tight tin partition to confine the water, which is conveyed to this wheel by two tubes consisting of mouth blowpipes cut off at the small extremity to attain an inside diameter of $\frac{3}{32}$ of an inch. These are placed through the edge of the case in such a way that the water from one strikes the paddles just a little below the axis, at an angle of 45 degrees to the horizontal plane of this axis, and from the other lower down and nearly parallel to this plane. The maximum effect is



attained when the stream strikes the centre of the paddle when the paddle is exactly at a right angle with the stream. Ordinarily it has been found necessary to employ only one stream of water. Ample provision must be made for the escape of the waste water. The fan is enclosed in a galvanised iron compartment, and somewhat resembles the tube with an inside diameter of $\frac{1}{2}$-inch. By attaching fan used by the blacksmith. It should have an outlet air a Y-tube to this, two blasts can be used as easily as one. A thick-walled rubber tube about $\frac{1}{4}$-inch in diameter has proved to be the most effective belt. The bearings must obviously be kept well lubricated to secure easy action.

Chemical Laboratory, Cornell College.

The Autoxidation of the Hydrocarbides from Coal-tar.—Max Weger.—The author has examined the modifications which take place on keeping these hydrocarbides purified in such a manner that they do not become coloured on contact with sulphuric acid. The experiments were carried out on trimethylbenzene, hydrindene, and tetrahydronaphthalene. After fifteen months all these products had become more or less changed, no matter how they had been kept, whether in ground-glass stoppered bottles, in sealed tubes, or in tubes simply closed with plugs of cotton-wool, either in the dark or exposed to sunlight. The specimens exposed to air and light are the ones that change the most; the phenomenon seems to be one of autoxidation, with the formation of acids.—*Berichte*, vol. xxxvi., p. 309.

THE MAZZA SEPARATOR FOR GASES.*

By Capt. VITTORIO CALZAVARA,
Technical Manager of the Società Civile Veneta per l'Industria del Gas ed Elettricità, Editor of the Monthly Technical Review *Il Gaz.*

THE applications of centrifugal force for the separation of liquid substances forming a compound mixture have, for some time, made their way in the industrial world, and many apparatus are based on this principle, as, for instance, the *Alpha* milk-skimmers. But, up to quite recently, it was not deemed possible that centrifugal force could succeed in separating gaseous molecules composing a mixture, and in grouping the same in strata, varying according to their density.

Signor Edoardo Natale Mazza, formerly an officer in the Royal Engineers of the Italian Army, has solved the problem. After having surmounted many obstacles, and conquered much diffidence, Signor Mazza has succeeded in demonstrating practically, that by means of his Separator gas molecules of different density, united in a mixture, are separated and grouped together in concentrical strata by the action of centrifugal force.

The Separator is a very simple machine, by means of which, and with the sole action of centrifugal force—therefore *mechanically*—the various components of gaseous mixtures are separated. This machine, as is shown by a drawing, consists essentially of a drum, revolving with great velocity, and into which the gaseous mixture to be treated is sucked in, in consequence of the rotation; the components, divided by the different effects produced on them by the centrifugal force, according to their various densities, escape by different outlets, and are forced by the same separating energy to follow their various destinations.

The separation of the gaseous elements takes place with greater or lesser facility, according to the greater or lesser difference in density of the components of the gaseous mixture; but in every case the result obtained is most noteworthy, even when the difference in density is small. In fact, atmospheric air which, as is known, is composed of oxygen and nitrogen, that is to say, of elements the density of which differs but slightly, centrifugated by the Mazza Separator has yielded at the periphery a quantity of air so far enriched in oxygen as to serve regularly to improve the fuel of the steam-boiler grates.

We have precise data as to the regular working, during several months, of the Separator, as for instance at the works of Hofmann and Co., Turin, where, according to the certificate delivered by this firm, the coal consumed by them has shown an average economy of 16 per cent, as against the consumption of fuel for the same boilers without the apparatus; at the paper manufactory of Messrs. Sezzano, at Bettole Sesia, where the saving has reached 22 per cent; and at the Turin Glue and Manure Co.'s works, where during three months working with the Separator, an increase in the yield of fuel attained 23 per cent.

Before the apparatus entered the industrial world, it had been the object of technical study and experiments; Mr. Robert P. Bethell, C.E., of Jarrow, England, the Società Italiana del Gas, in Turin, Prof. Benedetto Porro, of Turin, Prof. Dr. Schaefer, of Charlottenburg, besides others, after having made experiments at different places, at various epochs, and under different circumstances, each and all obtained such results as to enable them to testify to the success of the Separator, and to deliver precise and explicit declarations.

The Imperial German Patent Office granted Signor Mazza letters patent on the strength of Prof. Schaefer's report, and we consider it interesting to quote the words with which his report terminates:—

"It is the first time that, by means of Signor Mazza's invention, one has really succeeded in applying the known process of centrifugal force to gases with the result, up to now unforeseeable, that even with a moderate velocity of rotation, the quantity of oxygen in the atmosphere is increased at the periphery. The problem is thus in principle solved, and results have been obtained which are worthy of note, both from a scientific and a technical point of view."

Mr. Robert P. Bethell has certified:—"That the experiments prove conclusively that the machine is capable of increasing the amount of carbonic acid, sulphuretted hydrogen, and oxygen gases at the top outlet, such being the claims put forward by the patentee."

From a purely chemical standpoint, the results of the Separator have likewise been confirmed, and we may quote what Prof. Porro, who has made a great number of analyses of air centrifugated with the apparatus, wrote to Signor Mazza on the 18th of July, 1902:—

"Having already made a great number of analyses, I have become intimately convinced that your apparatus serves to centrifugate and to separate gases, and that the components of atmospheric air likewise undergo this physical law of centrifugation, and that the air is sensibly enriched with oxygen at the peripheric part of the apparatus to such an extent as to give good practical results."

Another ascertainment of special value, and particularly worth mentioning, is the report of the special Commission appointed by the Ministry of Marine of the Kingdom of Italy, to investigate and report on the practical results of Signor Mazza's apparatus. This Commission, after having made experiments under the severest control and the most careful surveyance, ascertained the following three very important results:—

1. That by using air centrifugated by the Mazza apparatus at a pressure of 4—5 atmospheres, 1 kilogrm. of New Pelton Main evaporated 12—15 kilogrms. of water.

2. That the quantity of ashes and cinders was *one-half* that of the same fuel when ordinary air was used.

3. That during the experiments, the temperature of the products of combustion, shortly before leaving the discharge outlets, was higher by 16° than the temperature which is to be ascertained in combustion under ordinary circumstances.

In consequence of this report, the Royal Ministry gave the order for an apparatus destined for the Taranto Arsenal.

Considering, however, that the industries, the representatives of which have met here, are of a special kind, we shall occupy ourselves more particularly with the applications of the Separator to the gas industry, after having made some brief general remarks.

Centrifugal force applied to industrial gaseous mixture, such as lighting-gas, water-gas, &c., becomes perceptibly manifest at an angular velocity of 300 revolutions per minute, with a radius of rotation of 40 c.m., provided the mechanical action does not last less than thirty minutes. By increasing the angular velocity, one can reduce the time of subjection to centrifugal force, without however, going below twenty minutes; thus, with this element of time, and with the angular velocity carried up to 1000 revolutions per minute ($r = 0{\cdot}40$), the best results are obtained in separating the above-mentioned components of industrial gases.

In centrifugating lighting-gas, one must bear in mind that a too energetic centrifugal action seems to exercise a certain influence on the composition of some of the richer carburets, or, rather, it seems to alter their illuminating power; we would therefore advise, as more convenient for industrial purposes, in this special case, the centrifugal force, resulting from the formula—

$$\frac{25 - 2}{0{\cdot}40} = \frac{V}{r} = F.$$

Another remark to be made is that concerning the special affinity manifested by some gases, and not justified either by the force of diffusion, or the force of gravity, which is precisely that which produces the phenomena of centrifugal force. In fact, by mixing on the one hand, in

* Memoir presented at the Congress of the Deutscher Verein von Gas- und Wasserfachmaennern, Zurich, June, 1903.

equal proportions, carbonic acid, oxygen, and nitrogen, and on the other, carbonic acid, carbonic oxide, and nitrogen, and applying the action of centrifugal force in identical conditions, the CO_2 of the *second* mixture separates with greater difficulty than that of the *first* mixture, whereas the difference in density should be more sensible in the second mixture, CO being, as is known, less dense than O. It would appear from this that a special affinity causes the molecules of CO and those of CO_2 to commix.

With regard to these, and other special affinities to be encountered, we may mention the force of diffusion of molecules or molecular velocity, which has often been put forth as an insurmountable obstacle to the solution of the problem of dividing the components of given gaseous mixtures *mechanically*.

First of all, we must bear in mind that the force of diffusion, or the impulsion of molecular velocity, takes place in every direction, and with the same intensity, presenting, therefore, as a geometrical place of action, a sphere. Now, if a given molecule thus moved is considered as also subject to a new force, acting, however, in a determined direction, there will evidently be a tendency towards a displacement of what results from the sole impulsions due to the force of diffusion. We get an idea, however rough, of this by observing the mode of acting, as well as the phenomena of rarefaction and compression which centrifugal ventilators present; but this is even better shown by the phenomenon, often noted, of gas mixtures of divers densities, as, for instance, water-gas, which, left for some time to rest in the gasometer, gets *stratified* to a most perceptible extent, in accordance with the law of gravity.

(To be continued).

NOTICES OF BOOKS

Thirty-ninth Annual Report on Alkali, &c., Works. By the Chief Inspector. Proceedings during the Year 1902. London: Eyre and Spottiswoode. 1903. Pp. 193.

The number of works now registered under the Acts in England, Ireland, and Wales is 1044. Of these, 75 only are works decomposing salt, while the remainder, 969, carry on processes which are scheduled under the Acts of 1881 and 1882. These numbers show a reduction of 8 alkali works, and an increase of 16 scheduled works in 1902. There are also 124 works registered in Scotland, bringing the total number of works registered in the United Kingdom to 1168. There were 4946 visits to works, and 5091 tests made during the past year, and it is very satisfactory to observe that no proceedings have been entered during the year for recovery of penalties for the infraction of limit clauses under the Act of 1881, or for failure to use the best practicable means for the prevention of the escape of noxious and offensive gases.

The Chief Inspector regrets that he has to report year by year, that success has not followed the various proposals made for reducing the acid escapes from the exits of the Chance-Claus process. He has, however, every reason to hope that experiments now in progress to reduce the escape of acid gases will turn out to be successful; before many months have elapsed all the data should be worked out, and he trusts that by then all the difficulties, of which up to now surprisingly few have presented themselves for solution, will be overcome.

The average escape of acids of sulphur and nitrogen from exits of sulphuric acid works, in which this manufacture is carried on by the lead-chamber process, is still maintained at a most satisfactory level, indicating the constant care and attention that are devoted to the conduct of this manufacture. The average escape from the 209 exits tested varies but slightly from the figures already given for 1900 and 1901.

Through the courtesy of manufacturers, the Chief Inspector is enabled again to give the figures showing the production of ammonia from all sources in the United Kingdom. These figures show a steady increase year by year, the most important contributor being, of course, the gas industry.

With regard to salt works, the limit escape of hydrochloric acid allowed is one-fifth of a grain per cubic foot of escaping gases; the average escape slightly exceeds one-fourth of this.

The conditions of trade have not been conducive to the renewal of activity of arsenic works in Devon and Cornwall, but the escapes of arsenic from this class of works have, on the whole, been low, and the works themselves maintained in satisfactory condition.

Tar works remain by far the most widely spread process whose supervision was added to the inspecting staff by the Act of 1892; the number of works remaining, as in last year, at 128. No modification of importance in the processes employed during the year calls for any comment.

CORRESPONDENCE.

THE SCIENTIFIC IMAGINATION.

To the Editor of the Chemical News.

Sir,—In the recent newspaper discussion of the hypothesis of Sir William Crookes, Sir Oliver Lodge, and others, concerning the constitution of matter, I have been quoted occasionally as a somewhat scornful opponent of the new ideas. Since these reports by no means represent the subject in a true light, I venture to write this letter in order to correct the misunderstanding.

A quotation from Sir William Crookes's article, which is now accessible to all, in the issue of *Science* for June 26th (see Chemical News, vol. xxxvii., p. 281), will perhaps most easily clarify the case. He says:—

"Indulging in a 'scientific use of the imagination,' and pushing the hypothesis of the electronic constitution of matter to what I believe to be its logical limit, we may be, in fact, witnessing a spontaneous dissociation of radium, and we begin to doubt the permanent stability of matter. . . . It must never be forgotten that theories are only useful so long as they admit of the harmonious correlation of facts into a reasonable system. . . . Are we not incessantly learning the lesson that our researches have only a provisional value? A hundred years hence, shall we acquiesce in the resolution of the material universe into a swarm of rushing electrons?"

The conditional statement and frank interrogation, appearing in this final climax of his, place him in a very different position from that to be inferred from the daily papers. Here is no claim to a great discovery, but merely the statement of the possible consequence of pushing an avowedly hypothetical inference to its logical extreme, with full recognition of the likelihood of its fallibility. With such an attitude no reasonable person can quarrel. The hypothesis that the hypothetical atom is divisible—and this is the particular proposal which has caused so much excitement—is, indeed, not unreasonable: but it is not the only possible explanation of the facts. In view of this circumstance, and also of the very recent discovery and the surprising nature of some of the phenomena concerning radium and the Röntgen rays, it seems to me premature to own unswerving allegiance to any definite interpretation at present.

The popular discussion of this question, as of so many scientific questions, has been much confused by the inability of many writers to distinguish between fact and hypothesis; and it was against this confusion that I argued in the interview which led to the exaggerated report. Facts are determined by observation and experi-

ment, and their truth depends only upon the accuracy of the observation and experiment. Their discovery is a lasting addition to the knowledge of mankind. On the other hand, hypotheses are attempts to interpret the facts; and many hypotheses, from their very nature, can never be proved. Although usually transitory, they are often very useful in suggesting further experimentation; but they become dangerous when mistaken for realities. Faraday, one of the greatest of scientific discoverers, dreamt many such scientific dreams; they were his leading inspiration, and they never harmed his work, because he always recognised their true place. In the same way, these new inferences concerning the reasons of the remarkable behaviour of radium may be highly suggestive and therefore valuable, if their inevitable limitations are always borne in mind.—I am, &c.,

THEODORE WILLIAM RICHARDS.

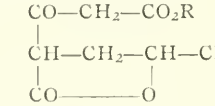
Peterboro', N.H., July 2nd, 1903.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 1, July 6, 1903.

New Syntheses effected by means of Molecules containing the Methylene Group associated with one or two Negative Radicles. Action of Epichlorhydrine on Sodium Acetonedicarbonic Ethers.—A. Haller and F. March.—In a previous research the authors show that, amongst the products of the reaction of epichlorhydrine on the acetonedicarbonates of methyl and ethyl, compounds can be isolated having the formula—



These substances are of the nature of chlorated ketoacetones and ether salts, which give with semicarbazide perfectly crystallised compounds. The authors now continue their researches on these complex molecules, and succeed in etherifying them by opening the lactic chain. The new compound thus obtained gives no precipitate with copper acetate, and does not combine with semicarbazide. These facts show that the ketonic function has disappeared, and that the complex $-CO.CH_2CO_2R$ has been modified.

Simplification of the Analysis of Silicates by the Use of Formic Acid.—A. Leclere.—The separations made during the analysis of silicates have long been known to be incomplete. The author finds that the difficulties arise from the acid employed for the solution of the silicate and for the formation of basic salts. The molecular weight of the acid is of great importance, and nitric acid—though of low molecular weight—is not so low as that of formic, the latter being therefore preferable in these analyses.

Conditions of Production and Stability of Hyposulphurous Acid.—J. Aloy.—Hyposulphurous acid can be rapidly produced by the action of an alcoholic solution of sulphurous acid gas on sulphur. The presence of alcohol and of neutral salts increases the stability of hyposulphurous acid, whilst the presence of acids and the action of solar light aids its decomposition. The mode of decomposition of the acid depends on the proportion of sulphurous acid existing in the solution.

Etherification of Hydracids.—A. Villiers.—When a mixture of hydracids and alcohol attains an equilibrium corresponding to a definite temperature, and is then allowed to cool, various modifications take place. The slowness with which these variations are produced, and that with which hydrochloric acid is etherified, does not allow of a complete investigation of this matter, but the results actually obtained by the author show the direction in which the reaction is tending.

Dibrom-acetylene. Purification; Cyroscopic Analysis.—P. Lemoult.—By the action of alcoholic potash on $CHBr=CBr_2$ and fractionation at the moment of preparation, pure dibrom-acetylene is obtained, of which the molecular complexity and the position of the bromine corresponds to the formula $CBr\equiv CBr$. The author proposes to continue his researches on this subject.

Lactose.—Em. Bourquelot and H. Hérissey.—Lactose accompanying emulsine, emulsine without lactose, and finally lactose without emulsine, are found in certain plants. All these facts are in agreement with the hypothesis of the individuality of the two ferments.

Action of Sodium on Carbon Tetrachloride and Chlorated Benzine. Formation of Triphenylmethane and Hexaphenylethane. — Jules Schmidlin. — Tetraphenylmelthane is a hydrocarbon of a very simple structure, and of great stability, judged from its chemical and thermo-chemical properties. It cannot be obtained by one of the simple methods used for the synthesis of hydrocarbons. The action of aluminium chloride on benzine and carbon tetrachloride gives only triphenylmethane. Carbon tetrachloride and chlorated benzine treated with sodium give diphenyl, and a mixture of hydrocarbons, amongst which the author isolated and identified triphenylmethane and hexaphenylethane in small quantities.

Preparation of Primary Alcohols by means of the corresponding Acids.—L. Bouveault and G. Blanc.—The authors generalise the method of reduction described in a recent paper (*Comptes Rendus*, vol. cxxxvi., p. 1676). The method applies as well to acids of small molecular weight as to those higher in the series, but, in these cases, as in the last research, serious experimental difficulties have to be overcome. The ethers of benzoic acid and of its homologues with carboxyl substituted in the radicle, are up to the present time the only ones with which the reduction does not take place.

β-Cyclohexanediol-1.2-ethylene Oxide and its Derivatives.—Leon Brunel.—During the preparation of β-orthocyclohexanediol there is a transitory formation of an ether oxide. The author examines this ether oxide and finds on analysis that it possesses the formula $C_6H_{10}=O$. He also prepares certain compounds of this ether oxide, formed by the action of hydrogen, water, and sodium bisulphite on it.

Heat of Neutralisation of Hydroferrocyanic Acid. Heat of Formation of its compounds with Ether and Acetone.—MM. Chrétien and Guinchant.—Hydroferrocyanic acid absorbs vapours of different organic compounds, such as ether, acetone, ethylene oxide, epichlorhydrine, and allylic alcohol. The authors determine the heats of formation of compounds of this acid with ether and with acetone, by decomposing them with dilute potash in a calorimeter. They find that the compound of a molecule of solid hydroferrocyanic acid, with ether vapour, evolves 11 calories for each molecule of ether fixed, and with acetone vapour, 9·7 calories per molecule of acetone fixed.

Bulletin de la Société Chimique de Paris. Series 3, Vol. xxix., No. 4.

The Constitution of the Electrolytic Peroxides of Lead, Nickel, and Bismuth.—A. Hollard.—Already inserted in full.

A so-called Electrolytic Reduction of Chlorate of Potassium.—André Brochet.—A controversial paper in which the author criticises the results published by Mr. C. R. Burrows and Prof. Bancroft, on a process for the electrolytic reduction of chlorate of potassium.

The Oxalomolybdites. — G. Bailhache. — Already noticed.

The Solubility of Gypsum in Solutions of Sea-salt. —Ch. Cloëz.—The author has obtained the following results in his experiments on the solubility of gypsum in solutions of sea-salt :—

Weight of NaCl in 100 c.c. of water.	Weight of gypsum dissolved.
Grms.	Grms.
0·0	0·2
2·44	0·635
4·77	0·826
9·50	1·056
14·22	1·193
23·15	1·275
31·3	1·583

Thus the solubility of gypsum in solutions of chloride of sodium increases in a regular manner with the concentration of these solutions. The determinations were made at a temperature of 14° on solutions remaining in contact for three months with an excess of pure hydrated sulphate of lime, the solutions being stirred up every day.

Experiments on Plaster-of-Paris; Baking the Gypsum.—Ch. Cloëz.—It was found by experiment that anhydrous plaster-of-Paris absorbs moisture when exposed to the air :—

In	1	hour it absorbs	..	..	3·70	per cent of	water
,,	2	hours	,,	.. ..	4·27	,,	,,
,,	3½	,,	,,	.. ..	5·70	,,	,,
,,	19	,,	,,	.. ..	7·57	,,	,,
,,	27	,,	,,	.. ..	7·77	,,	,,
,,	74	,,	,,	.. ..	7·93	,,	,,

The above experiments were carried out at 14—16°. At a lower temperature the absorption takes place more slowly, but it reaches the same limit. Anhydrous plaster, which is very easy to prepare, is an excellent dehydrating material, by which means alcohol can be brought easily from 90° to 98°.

MISCELLANEOUS.

Australasian Association for the Advancement of Science.—The tenth meeting of this Association will be held at Dunedin, N.Z., from the 6th to the 13th January, 1904, under the presidentship of Prof. T. W. E. David, M.A., of the Sydney University. The chairman of the local council will be the Right Rev. Dr. Nevill, Bishop of Dunedin. The presidents of the various sections will be as follows :—A., Astronomy, Mathematics, Physics, and Mechanics—Prof. W. H. Bragg, M.A. ; B., Chemistry—J. Brownlie Henderson ; C., Geology and Mineralogy—W. H. Twelvetrees, F.C.S. ; D., Biology—Col. W. V. Legge, R.A. ; E., Geography—Prof. J. W. Gregory, D.Sc., F.R.S. ; F., Anthropology and Philology—A. W. Howitt, F.G.S. ; G1., Social and Statistical Science—(not yet filled) ; G2., Agriculture—J. D. Towar ; H., Architecture, Engineering, and Mining—H. Dease, M.A., M.Inst.C.E. ; I., Sanitary Science and Hygiene—Dr. Frank Tidswell ; and J., Mental Science and Education—John Shirley, B.Sc. In addition to the meetings of the sections, arrangements are in progress for various entertainments, and for excursions to places of interest in the neighbourhood of Dunedin and to other parts of the colony. Further particulars can be obtained from the Hon. Local Secretary, Geo. M. Thomson, 129, Moray Place West, Dunedin, N.Z.

Institute of Chemistry.—July Examinations, 1903.—Examiners in Chemistry—Walter William Fisher, M.A. (Oxon.), F.I.C. ; Prof. William Palmer Wynne, D.Sc. (Lond.), F.R.S., F.I.C. Examiner in Therapeutics, Pharmacology, and Microscopy—Arthur Pearson Luff, M.D. (Lond.), B.Sc. (Lond.), F.R.C.P., F.I.C. The following Candidates passed :—

Intermediate Examination.—James Alexander, Glasgow and West of Scotland Technical College ; David Allan, Glasgow and West of Scotland Technical College ; Harold Frederick Barke, Owens College, Manchester ; James William Brisbane, King's College, London ; John Alexander Campbell, Glasgow and West of Scotland Technical College ; Arthur Charles Carter, University College, London ; Reginald William Lane Clarke, Finsbury Technical College, London ; Bertie James Eaton, Finsbury Technical College, London ; James Dick Fraser, Glasgow and West of Scotland Technical College ; James Stuart Hills, King's College, London, and the School of the Pharmaceutical Society, London ; Leonhardt Erich Hinkel, King's College, London ; Charles Edgar Male, King's College, London, and the School of the Pharmaceutical Society, London ; James Miller, Yorkshire College, Leeds, and under W. McD. Mackey, F.I.C. ; Russell George Pelly, Finsbury Technical College, London ; Louis John Eczekiel Riley, Glasgow and West of Scotland Technical College, and the University, Edinburgh ; Walter Charles Scott, Finsbury Technical College, London ; David Spence, Glasgow and West of Scotland Technical College.

Final Examination for the Associateship (A.I.C.).—Branch "A" (Mineral Chemistry).—Alfred Vincent Elsden, University College, London ; Leo Frank Guttmann, Ph.D. (Heidelberg), A.C.G.I., Central Technical College, London, and the University, Heidelberg ; James Stewart Kerr, Assoc.R.C.Sc. (Lond.), Royal College of Science, London ; Harold George Lacell, Assoc.R.C.Sc. (Lond.), Royal College of Science, London ; Frederick Peacock Leach, Assoc.R.C.Sc. (Lond.), Royal College of Science, London ; Henry Stanley Raper, B.Sc. (Vict.), Yorkshire College, Leeds ; Ewing Smith, Glasgow and West of Scotland Technical College ; George Steedman, Glasgow and West of Scotland Technical College. Branch "B" (Metallurgical Chemistry).—William Harold Keys, Birmingham University. Branch "D" (Organic Chemistry).—Walter Geoffrey Black, A.C.G.I., Central Technical College, London ; James William George Brooker, Finsbury Technical College, London ; Hamilton McCombie, M.A. (Aberdeen), Assoc.R.C.Sc. (Lond.), Aberdeen University, and the Royal College of Science, London ; Sidney Scrivener Napper, A.C.G.I., Central Technical College, London ; George Tattersall, B.Sc. (Lond.), University College, Nottingham ; Henry Lucas Wall, Finsbury Technical College, London. Branch "E" (Analysis of Food and Drugs, and of Water, including Examination in Therapeutics, Pharmacology, and Microscopy).—John Frederick Percival Fielding, King's College, London ; Harold Adams Scruton, B.Sc. (Lond.), Yorkshire College, Leeds ; Thomas Edward Wallis, B.Sc. (Lond.), School of the Pharmaceutical Society, London.

For the Fellowship (F.I.C.).—John Don, M.A. (Aberdeen), B.Sc. (Lond.), Aberdeen University.

Nerol : A New Alcohol found in Essential Oils.—H. von Soden and O. Zeitschel.—Nerol is a new terpenic alcohol resembling geraniol, and forming part of various essences. To isolate it, the essence is saponified in the cold with alcoholic potash ; the oil remaining is washed with water and distilled in vacuo ; two fractions are obtained, one of linalol and terpenes, and the other of terpeneol, geraniol, and nerol. These two latter alcohols are transformed into acid phthalic ethers, which are isolated and then saponified ; in this manner we obtain a mixture of geraniol and nerol, which can be separated by adding powdered chloride of calcium, and washing with petroleum ether ; geraniol gives an insoluble solid compound with chloride of calcium. The nerol passes into the petroleum ether, which is distilled, washed, and rectified. The return is 2 per cent. Nerol is a liquid having the composition $C_{10}H_{18}O$; its boiling point is 225—227°, and its density at 15° = 0·880 ; it has an odour of roses, much fresher than that of geraniol. Its acetate boils at 134° under 25 m.m., and its density at 15° is 0·917 ; the formate boils at 119—121° under 25 m.m.—*Berichte*, vol. xxxvi, p. 265.

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The Examination will extend over four days, and may be Theoretical, Practical, Written, and Oral. The Syllabus will include Biological Chemistry, with special reference to the Chemistry and Bacteriology of Foods, Water, Sewage and Effluents, and the practical applications of Biological Chemistry to Industries.

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2281.

THE ACTION OF SALTS OF RADIUM UPON GLOBULINS.

By W. B. HARDY.

Two solutions of globulin from ox serum were used, one electro-positive, made by adding acetic acid, the other electro-negative, made by adding ammonia.

They were exposed in shallow cells, one wall of which was made of thin mica, to the radiations from 50 m.grms. of pure radium bromide, enclosed in a capsule covered with mica, so that two sheets of mica were interposed between the radium and the solution. No action took place in one hour.

The globulin was then exposed as naked drops, separated by 3 m.m. of air from the radium salt, with suitable controls, shielded from the radium.

In the + solution the opalescence rapidly diminished—that is to say, solution became more complete. The − solution was turned to a jelly, at first transparent, rapidly becoming opaque. The action was complete in about three minutes.

Radium, like other radio-active bodies, gives off matter in three states—(1) an emanation having the mobility of a heavy gas, (2) positively charged particles of little penetrating power, and relatively large size, (3) ultramaterial negatively charged particles, of a size much smaller than atoms. A mica plate will screen off 1 and 2, therefore the globulin solutions are unaffected by the ultramaterial negative particles. The rate of action and conditions of the experiment make it unlikely that the emanation was the active agent, though, owing to its nature, intense solvent or coagulating power may safely be predicated of it. The action observed was almost certainly due to the + particles. These are of material dimensions.

Globulin systems therefore seem to be completely transparent to the ultramaterial electrons, and so too, probably, are the living tissues, since the physiological influences of the discharges from radium seem to be limited to a superficial layer a few m.m. deep.

The experiments were carried out by the kindness of Sir William Crookes in his laboratory, and with his assistance. —*Proceedings of the Physiological Society*, May 16th, 1903.

CHLORINE SMELTING, WITH ELECTROLYSIS.*

By JAMES SWINBURNE.

(Concluded from p. 66).

Capital Cost.

As regards capital cost, it is difficult to say how much the plant for any particular case will cost, as it depends on the ores to be smelted and local conditions. It is therefore wise to allow a large margin on all the plant of a new description, and a large margin is left in the 30s. a ton for depreciation, repairs, &c.

The electrical generating plant is a different matter, however. A large installation may be taken at an outside figure of £25 per kilowatt, including buildings and spares. In this case, there is no accidental overloading, as in light and power distribution stations, so that £25 a kilowatt includes spares by overloading and separate plant.

It will be evident that the cost of generating plant is a consideration in the capital expenditure. In the case of water power at 0·086, the capital expense is borne wholly by the owners of the power station. The power is there, and if it is not used for one purpose, it is used for another, so that the water-power company really takes no special risks involved in a new process. The 0·086 thus covers the capital of the water station, and no water-power capital figures in the process accounts. A given amount of available capital thus gives much better results on a water power.

In the case of a gas plant, the owners of the process may put up their own plant.

The capital cost of gas generating plants may perhaps be safely taken as £25 a kilowatt, but it must be borne in mind that there is more uncertainty about it, and more chance of its becoming antiquated soon. Improvements in gas generators and engines are more rapid than in steam just now.

In the case of steam generating plant, the same considerations come in. If the owners of the process put down their own plant, they must allow for high profits on a share of it. Though 0·25 is given as the cost of steam-generated electrical energy, that is only if there is no risk. No business men would put down a generating plant specially to supply us with nothing but a guarantee of 0·25 per kilowatt hour for a year or two. The nearest approach to such a case is a power station such as those being put up in various districts now. Even one of them would not contract for 0·25, as an output of some thousands of kilowatts day and night means adding special plant which, if thrown out suddenly by the financial failure of the process, would have to be idle till the demands of the station caught up with it, and even then the dynamos would have to be altered. In buying energy from a modern power station, without contributing to the capital, the price would probably be about 0·3 per kilowatt hour.

If the process owns its own steam generating plant, it would be safe to allow for part of the cost being covered by 5 per cent debentures.

The idea of risk profits is this :—Any new process such as this, however satisfactory the results so far, involves risks of failure. There are many chances of difficulties in working on a still larger scale, and chances of new and better processes coming out. The last chance is probably small, because the various problems of smelting copper, lead, zinc, antimony, tin, &c., have all been before the world for many years, and a new process that bids fair to solve all of them in a new way is not likely to be superseded as regards many of them by something else, though it might be as regards one of them. The only real risk is that of all new processes—unforeseen difficulties or expenses. The present process is too far advanced to leave many loopholes, but even then experience of other industries shows that it is not wise to embark in a new scheme unless, after the most searching criticism, the profits on paper are so large as to leave a very wide margin. But to get a fair idea, it is obvious that capital in steam-generating plant, or in sites, must not all be counted in as expecting what are here called risk profits.

One kilowatt, at 4 volts per cell, deposits 2·61 tons of zinc a year at a current efficiency of 1. The departure from this current efficiency is minute ; but the pressure will probably be reduced considerably with larger vats. Steam plant for a ton of zinc a year thus costs £9 12s., or roughly £10 in capital. To reduce a ton of lead a year by replacement with zinc thus involves a capital of £3, and a ton of copper (cuprous) £5 approximately.

In metallurgy it is usual, and some people find it convenient, to work in "units." For each ton of ore smelted per year, the capital cost of steam plant thus comes out—zinc £0·1 per unit, copper £0·05, lead £0·03 approximately ; so that if an ore has 33 units of lead, 20 of zinc, and 10 of copper, and plant is wanted to smelt 100,000 tons a year, the steam plant would cost £350,000.

As to smelting plant, including vats, transformers, agitators, pumps, boiling-down plant, and buildings for all the works other than the generating plant, it may be wise to allow as much as half the steam plant for cost of

* A Paper read before the Faraday Society, June 30, 1903.

process, plant, &c., and another equal sum for working capital.

To begin with, we may work out a rough estimate for treating Bluestone ore in this country, with steam generating plant put up for the purpose. 100,000 tons of ore a year will be taken, the ore containing, as delivered, 22 per cent zinc, 18 per cent lead, iron 4 per cent, manganese 3 per cent, gangue 35 per cent, sulphur 18 per cent, silver 15 ozs. The process would require a capital of roughly £550,000, including the generating plant, with no debentures. This allows nothing for payment of patent rights.

The cost of working would be :—

By 100,000 tons of slimes delivered at £2 10s.	£250,000
„ 100,000 tons of ore carried through process, excluding cost of energy..	150,000
„ Electrical energy	94,200
„ Allowance for loss of metals and chlorine, say	15,000
„ Cost of realising products	16,000
	£525,200
Profits	341,200
To sales of zinc at £20, lead at £12, silver at 2s., two-thirds of the sulphur at £3, iron oxide at £2, manganese £5 5s.	£866,400

This leaves over 60 per cent profit on capital, a profit which would leave a margin even after paying the royalties wished for by the proprietors of the patents.

Suppose, however, energy were bought at no less than 0·4d. per kilowatt hour from a power-supply station. The costs would be increased by £55,800 per annum. But the capital would be reduced to, say, £275,000, making a profit of £285,000 on £275,000, or over 100 per cent.

Another estimate may be taken for different conditions. In this case a water-power works on the waterway from the American lakes to the sea will be considered, dealing with ore from the district above.

Take the ore at zinc 41, lead 15, and silver 2 ozs. This is a real ore, but I have no data as to iron contents. If there is any iron to speak of, there must be little gangue. Also I do not know the value of this ore, but will assume it to be refractory. It will then give a good miner's profit if the ore is taken at £2 a ton delivered on the works. To smelt 100,000 tons a year of such a rich ore as this would need about £500,000, of which half is process plant and half working capital. Electrical energy would be bought at, say, 0·1d. per kilowatt-hour.

100,000 tons Canadian ore smelted in America by water-power :—

By 100,000 tons ore	£200,000
By process expenses..	150,000
By electrical energy	73,500
By losses, commission, &c. ..	30,000
	£453,500
Profits	566,500
To sales of metals	£1,020,000

There is thus well over 100 per cent profit on this scheme—of course before paying royalties.

This ore has very little gangue, and in that case it might be worth while to dilute it with poor copper ore, especially if the copper ore contains some other valuable metals, such as zinc, antimony, nickel, or precious metal. Thus if the ore has only 10 per cent of gangue, and a low-grade copper with 3 per cent of copper, 5 per cent of zinc, and 5 per cent of iron, has some 80 per cent of rock; for every ton of the rich ore more than a ton of this poor ore could be run through too. The works would then deal with 100,000 tons of this poor ore with very little extra capital cost or expense, as it is nearly all rock, which is eliminated near the beginning of the process. A little more than £1 10s. a ton for the process should have been allowed for the rich ore, and a poor ore takes a great deal less.

Discussing the different metals in order :—

Antimony.—This metal is very easily extracted from the sulphide, either as brown sulphide or as oxide, preferably as oxide. It can also be got out as regulus by reduction. It does not matter whether the antimony is mixed up with other metals or alone.

Arsenic.—This is almost on all fours with antimony. Like it, its sulphide is very easily converted into chloride. It can be equally easily treated when it is an arsenide of other metals. The chief difficulty of antimony and arsenic arises from the poisonousness of their volatile chlorides. We have done little with arsenic.

Bismuth.—This is a small question. Bismuth would be easy to deal with, as it falls out of solution as oxychloride.

Cobalt.—This comes out as oxide; if nickel is also present, the nickel and cobalt and iron, and perhaps manganese, have to be separated in the wet way. There is nothing special about the problem.

Copper.—This comes out of the transformer as cuprous chloride, which is soluble in the other chlorides. It is deposited as cement copper by zinc, not iron. The process will handle ordinary high-grade copper ores successfully, as any other metal, except iron or manganese, is extracted separately as metal too. The copper is of course free from sulphur, arsenic, iron, antimony, phosphorus, silver, &c. In fact, it is pure. Copper can be equally cheaply extracted from arsenical or antimonial ores; in fact, the ores may have arsenic, antimony, zinc, lead, iron, nickel, gold, silver, cobalt, or anything else, and they are all separately extracted without appreciable extra cost. Poor copper ores will either be concentrated or run in with other richer stuff.

Gold.—When present in copper, lead, or other such ores the gold comes out with the silver. Gold in conjunction with antimony, arsenic, tellurium, and small quantities (per ton) of common metals can be treated as a low-grade ore, and run in with any rich mixed or other sulphide, such as lead, zinc, or even rich copper ore or matte. It is largely a question of carriage, and what ores are near each other and near the works.

Iron.—This metal occurs in zinc and copper ores, and comes out as oxide. This oxide is reckoned at £2 a ton, and is useful as a paint. The value depends on the tint, and this depends on the way it is worked up, a matter we have not yet studied. Good oxide fetches high prices, up to £15 or £20 a ton, but the sale is probably very limited. Assuming the lowest price. £2 is not too much to count upon for paint for preserving iron structures where colour is not an object. The extraction of iron itself is a different question. It would come down as a powder from the fused chloride, and would have to be fused together. It would probably cost something under £10 a ton. It may prove that chemically pure iron, with no trace of phosphorus, sulphur, silicon, or manganese or other impurity, is well worth £10 a ton for making special steels or electrical iron stampings.

Manganese.—This metal, like iron, is a drawback in an ore, as it comes out as dioxide, which is not valuable, though the sale of the manganese from such an ore as Broken Hill slimes is worth considering.

Nickel.—This is much the same as cobalt as far as the process goes. It comes out of the transformer as nickel chloride.

Silver.—The silver comes out separately—that is to say, it is extracted from a lead ore as a rich lead-silver alloy. From copper ores it is precipitated by cement copper from the solution of the chloride. Or it may be thrown down by the Claudet method.

Tin.—Tin ores can be added to the charge of the transformer, or treated alone. There is nothing peculiar about it.

Zinc.—Has been fully discussed. Zinc need not exist in the ore worked.

As it is not possible to give a series of estimates for all the innumerable complex ores, it may be well to give an approximate rule which can be applied to any ore.

Rule for Capital.

For each ton of ore per annum to be treated allow :—

Zinc	£0·1	per unit
Copper	£0·05	,,
Lead	£0·03	,,

and for other metals which are extracted in the metallic state, in proportion, inversely as their equivalents. Metals like iron and manganese or antimony, which are extracted as oxides, do not count. This gives a very rough idea of capital necessary for process plant and working capital. If steam or gas generating plant is to be put down, double this capital.

Rule for Working Costs.

For each ton of ore treated at works allow cost of ore delivered, plus £1 10s. per ton for treatment, including everything but cost of electrical energy, and allow 5 per cent extra on cost of ore to cover all waste.

The cost of energy depends on the metal content and on the cost of generation. Steam may be taken at 0·25, gas at 0·125, and water at 0·1 penny per kilowatt hour.

Cost per unit of	Steam power. £.	Steam power. Pence.	Gas power. £.	Gas power. Pence.	Water power. £.	Water power. Pence.
Antimony (if as metal)	0·042	10	0·021	5	0·016	4
Copper	0·0175	4·2	0·009	2·1	0·007	1·7
Iron (as oxide)	—		—		—	
Manganese (as oxide)	—		—		—	
Lead (de-silverised)	0·0107	2·6	0·0054	1·3	0·0043	1
Nickel	0·038	9	0·019	4·5	0·015	3·6
Silver and gold	Inappreciable.		—		—	
Tin	0·038	9	0·019	4·5	0·015	3·6
Zinc	0·0342	8·2	0·017	4·2	0·0136	3·3

The price in pence is added because it gives cents too by doubling.

To find the value of the products, add up all the metals in full, the waste or loss being amply covered by the 5 per cent. The iron and manganese must be omitted, being oxides. Their market is uncertain, and much must not be allowed for them. Some of the sulphur is burnt; it is safe to allow for two-thirds of the sulphur contents of the ore at market price.

The process is thus anything but expensive. To see how this is the case, comparison must be made with other plants. Take a mixed zinc, lead, and copper ore, for example. If we take the corresponding plant on the present system, we have first a concentration plant; next a lead-smelting works with all its adjuncts, including a desilverisation plant; a zinc works and refinery; and a copper-smelting works with an electrolytic refinery. There can be no comparison as to capital cost. As to working cost, the new process begins by saving the concentration, except for very low-grade ores, or where carriage comes in, and thus saves waste. Though 5 per cent waste has been allowed, there is practically no waste of metals; there is nothing to correspond with the waste of copper, zinc, and lead in smelting. In addition, iron and manganese oxides are got out, and most of the sulphur is obtained as brimstone. In this process a smelting works is independent of ore supply, in the sense that it can work any ores.

If copper ores go up, it can devote its whole energy to zinc and lead, and so on, and the variety of ores is so great that the process cannot enhance the value of the ores to the miners. The supply of ores is thus practically unlimited.

This process is the joint invention of Mr. E. A. Ashcroft and myself. Mr. Ashcroft came on the scene when the process was in the baby or test-tube and patent stage. He took it up from that point, and has developed it, not without the necessary pecuniary food being provided for it, into a healthy, full-sized process which appears to have the backbone of a giant. Since he joined we have worked together as co-inventors, and he has designed and worked out all the plant and carried out all the works. Mr. Ashcroft has also read a paper on this process before the Institution of Mining and Metallurgy; but the process is so little known that it seemed advisable to offer a paper to the Faraday Society.

I hope no one will object to the introduction of questions of cost. This paper is largely financial. All engineering—electrical, chemical, or otherwise—is purely a question of cost. There may be people who think that Science is not Science unless it is merely useless information. Science really is not Science unless it is, or seems likely to be, of use. Every step of the inception and development of a process like this involves Science, and practically nothing but Science. I have also dwelt rather on the broad questions of the scope of its application than on details, because Mr. Ashcroft's paper goes into details very fully, and should be read with this. I am anxious also that the discussion should not turn on detail difficulties that speakers think we ought to meet, or the impossibility of getting off sulphur by replacement with chlorine, or of electrolysing zinc chloride on the large scale; because we have transformed and electrolysed on the large scale with perfect success. I am much more anxious to know the Society's opinions on the probable future of such a process as this, and its application to the various ores found in different localities.

My thanks are due to the Metallurgical Trust, Limited, the proprietors of this process, for leave to offer this paper to the Faraday Society.

ON THE LOSS OF SILVER IN ROASTING ARGENTIFEROUS BLENDE.

By G. SANDER.

When argentiferous blendes are roasted in Maletra or Liebig-Eichorn furnaces, a loss of silver occurs, concerning which we have had little or no exact data up to the present. We have therefore carried out the series of experiments given in Table I. By "loss on roasting" we mean the loss of weight sustained by the blende after roasting.

The proportion of the fixed compounds in the blende should thus increase proportionally to that loss. Table II. gives the percentage of the principal elements in the blende.

Table I.

Mark.	Loss on roasting. Per cent.	Loss in silver, grms. per ton. Before roasting.	Loss in silver, grms. per ton. After roasting.	Loss of silver. Per cent.
Blende MV	10·50	340	335	11·77
,, MP	10·05	413	410	10·68
,, F	11·25	230	227·5	12·15
,, C	12·70	324·5	330	11·22
,, A	12·00	375	375	12·00

Table II.

Mark.	Per cent. Zinc.	Sulphur.	Lead.	Iron.	Lime.	Magnesia.	$BaSO_4$.	Quartz
Blende MV	31·00	22·26	7·50	4·25	1·60	0·65	24·50	2·75
,, MP	41·80	27·40	4·00	3·00	1·40	0·80	10·55	10·20
,, F	43·93	24·95	7·35	5·20	0·10	0·15	—	15·46
,, C	47·50	33·26	2·15	13·60	—	1·20	—	1·14
,, A	42·60	29·07	8·75	7·50	0·12	1·10	—	10·00

The percentages of silver were determined in the following manner :—20 grms. of the oxidised mineral and 20 grms. of lead were fused together in an iron crucible, and the silver estimated in the lead separated. As by this method there may be losses of silver if the ore contains

sulphur, we added to the roasted ore the amount of sulphur lost by roasting, so as to obtain comparative results. This addition of sulphur varied from 4 to 6 grms, according to the composition of the blende. It was found, however, that this addition of sulphur was useless. The differences obtained by making the estimation with or without the addition of sulphur never exceeded 5 grms. of silver per ton of ore.

An examination of the last column of Table I. shows that the losses of silver are about the same, though the roastings were done at two different works. It must not be imagined, however, that the loss of silver is always 10 or 12 per cent of the amount present, for it depends above all on the temperature at which the furnace is maintained. This loss must be attributed especially to the volatilisation of the metallic silver formed, and it should be greater as the temperature of the furnace is higher.

The raw blende, as a rule, contains its silver in the form of sulphide; this latter is transformed into sulphate during the roasting, and, at the end of the operation, when the temperature has risen to over 900°, into metallic silver, sulphuric and sulphurous anhydrides, and oxygen.

A portion of the volatilised silver should be recovered in the dust chamber. In fact, dust has been recovered from these chambers containing 500 grms. of silver per ton, although the original blende did not contain even 250 grms. per ton.

These dusts contain also 25 per cent of lead, while the blende contained 9 per cent, showing that a portion of the lead, still undetermined, is also volatilised.

I will mention here that many points in connection with the roasting of blendes require examination from the chemical point of view, especially the manner in which lead, lime, and magnesia behave in the presence of silicic acid.

The proportion of sulphur does not only affect the zinc, but also the compounds of lead and silver in the residues.—*Zeitschrift für Angewandte Chemie*, 1902, p. 353.

THE MAZZA SEPARATOR FOR GASES.*

By Capt. VITTORIO CALZAVARA,

Technical Manager of the Società Civile Veneta per l'Industria del Gas ed Elettricità, Editor of the Monthly Technical Review *Il Gaz*.

(Concluded from p. 69).

There ought thus to be no difficulty in admitting that centrifugal force also, which by the will of man can attain a most important intensity, acting always by its nature on a plane, can succeed in separating gaseous molecules with divers masses.

Having premised as much, we shall now mention those applications which appear to us as most advantageous and surest in connection with the gas industry, which is the one of most interest to those who have attended this Congress.

The density of the principal components of lighting-gas varying greatly, as is known, and such variations happening within rather broad limits, we understand easily how the separation of the same by means of the Separator presented no difficulties; this separation was obtained in numerous experiments made at the works of the Società Italiana del Gas, in Turin, and as the indexes of density most approximate among each other, of the principal components of lighting-gas (depurated from hydro-sulphuric acid, ammonia, and cyanogen) can easily be grouped in two principal large divisions, we shall see how their grouping occurs, when the mixture is subjected to centrifugation in the Separator.

We shall take as a basis a normal analyis of depurated gas, and the density of the air = 1.

	Density.	Volumes.
Benzole, C_6H_6	2·77	0·700
Propylene, C_3H_6	1·498	0·400
Olefiant gas, C_2H_4	0·9674	2·100
Carburetted hydrogen, CH..	0·556	37·600
Hydrogen, H	0·06926	46·300
Carbonic oxide, CO	0·9674	11·200
Carbonic acid, CO_2	1·529	0·800
Nitrogen, N	0·97137	0·900
	Total volumes	100·000

We see at once how, by applying centrifugal force to the mixture, the separation will occur between groups having the limits of density farthest, and that we shall therefore have at the central part the grouping of the gases CH_4 and H, the density which is much below the unit (0·556 and 0·6926 respectively), and at the peripheric part the grouping of all the others of which the limits of density vary between 0·9674 and 2·77.

This theoretical presumption has been, in fact, confirmed by the experiments made at the works of the Società Italiana del Gas, in Turin, as their formal declaration proves; it is therefore established that at the centre we shall find a gas almost completely free from heavy carburets which will gather at the periphery.

How can a gas company utilise these mixtures resulting from the separation in an industrial manner? There are numerous ways, and various criteria may be followed, according to the special convenience of each single company.

First of all, the gas collected at the centre may be utilised to great advantage, by carrying out economically the advice given by Lewes, whose great competency is well known, and who recommends us to introduce, by insufflation, hydrogen into the gas-conduits as it issues from the retorts, so as to draw on the heavy carburets which are abundant during the first hours of distillation, and which, as is known, deposit themselves in great quantity to the detriment of the illuminating power of the gas.

At present, on account of the heavy cost of hydrogen produced direct, gas-works adopt the insufflation of air or water-gas, and these diminish, on account of their presence, the increase of illuminating power which would be given by the greater quantity of carburets drawn on by the gas at the issue from the retorts.

It is evident that by employing the hydrogen extracted at a minimum cost from the gas itself with the Separator, the objection on account of the expense disappears, and it will be possible to apply Lewes's excellent advice on a large scale.

If one also consider how extensive to-day, as compared with the past, the use is of gas for heating purposes (kitchens, stoves, incandescent light), the process of separation by means of centrifugal force will bring about remarkable economical results; the increase of heavy carburets which with Lewes's process would be drawn on in the gas to be distributed, corresponds not only to an increase of illuminating power, but also to an increase of heating power; this has been recently shown, and is evident, if we consider that the calorific power of complex lighting-gas is 5500 calories per cubic metre, as against about 2800 calories in hydrogen; and as gas is always sold per cubic metre, we must only take into account the difference in calories with respect to the unit of volume.

There are besides several other *separations* which the Mazza apparatus has proved capable of effectuating easily, and some of these, according to the requirements and the special conditions of the various works, will certainly be adopted to great advantage.

It is thus possible to depurate lighting-gas completely from hydrogen sulphide and carbonic acid, and this has been already effectually done.

Another important use to which, according to the inventor, the air enriched with oxygen and collected at

*Memoir presented at the Congress of the Deutscher Verein von Gas- und Wasserfachmaennern, Zurich, June, 1903.

the periphery of the apparatus might be put, is the rapid and cheap revivification of all matters polluted by the epurators, by passing enriched air through these matters.

Gas companies will, of course, investigate this subject, and have experiments made most carefully; our opinion is, that this depuration could really be effectuated, because, although we are not aware of any such experiments having yet been made, the action of atmospheric hydrogen in such operations has been fully recognised.

As is known to all of us, for reasons over which we have no control, gas companies are now obliged to excogitate all means for utilising the nitrate products of their industry.

First of all, on account of a fact which is the natural consequence of an economical law, the price of gas has been reduced, and the profits formerly realised have been cut down, and great attention has been devoted in view of studying and finding out the best ways and means of utilising sub-products. On the other hand, the increased production, due to the reduction in price, has turned the small percentage of useful nitrogen, found in the immense quantities of coal used, into important quantities, which, as Mr. Boehm, C.E., once justly remarked, represent receipts by no means to be neglected.

Who does not perceive at a glance the immense advantage which the gas industry could derive by using the Mazza apparatus in the preparation of cyanides?

Another application of the Mazza Separator interests the gas trade, as well as all those whose industries need steam; the apparatus in question is specially and, in fact, exclusively suited to feed the steam boiler grates with air enriched with oxygen, by means of centrifugation. We consider it particularly interesting to call attention to this application of the Separator on account of the economical results obtained, as also because the success is beyond all doubt, from the simple fact that the results obtained are no longer experimental, but industrial ones.

The increased yield of fuel almost always reaches 20 per cent, and not seldom does it surpass this figure; the results have been obtained with apparatus which have been working regularly for months, and, as stated, in manufactories.

The greater yield of the fuel due to the action of the Separator can in no case be attributed to the apparatus considered as a *ventilator*, and this, above all, because feeding with *separated air*, there is constant aspiration under the grate (as is noted daily at Hofmann & Co.'s works, where there is a fluitometre), because the products of combustion are collected at the basis of the chimney, and show a temperature about 20 per cent lower than what they do when ordinary air is employed, and because the saving of fuel is a positive proof of a greater yield, whereas it is well known that the use of ventilators *diminishes* the yield.

It is therefore beyond a doubt that it is the *composition* of the air employed which produces the greater yield of the coal, as it is beyond a doubt that it is the Separator which, by its own action, changes the normal composition of the air in which oxygen, as burning substance, enters in a greater proportion.

We may, finally, mention some other applications of the Separator, the results of which the inventor declares as certain, and which we consider as most probable. Amongst these, the separation and extraction of fire-damp is one of the most remarkable; the danger, now always present, and the terrible results of the combustion of fire-damp in coal mines, would completely disappear by employing the apparatus.

There is also the separation of the products of combustion of carbonic oxide (density 0·9674) from carbonic acid (density 1·529), and the consequent utilisation of the former; experiments have been made most successfully, and anyone can understand the importance of this application in connection with water-gas, and Dowson gas, to be used in gas machines.

We will specially mention only what might be obtained by carrying out the separation of blast furnace gas, availing ourselves of a very important study on this subject by Signor Emilio Cortese, C.E.

Blast furnace gas is, on an average, composed as follows:—

	Volume.	Weight.	Air density = 1.
Nitrogen	60	58	0·96137
Carbonic oxide	24	24	0·9674
Carbonic acid	12	17	1·5290
Hydrogen	2	0·2	0·06926
Carburetted hydrogen, CH_4	2	0·8	0·5560
	100·00	100·00	

On coming out of the furnace the gases contain 8 per cent of water vapour, which can be, for the greater part, condensed in the epurators, and between 1 and 5 grms. of dust and powder per cubic metre. The gases, after cooling, are treated by the Separator, and we thus directly eliminate the remaining water vapour, the dust, and, most easily, the carbonic acid, at least for the greater part.

The light mixture would remain composed of nitrogen, carbonic oxide, and carburetted hydrogen; it would thus be considerably enriched by the suppression of at least 17 per cent of its weight in inert gas, and be freed from noxious elements.

It would serve much more efficaciously in motors, because it would not be so poor a gas as Dowson gas, and would be free from dust and powder, the effects of which are disastrous. We may add that, having a gas-generator or a fire-box with a grate at hand, the carbonic acid can be brought in contact with the fuel, and reduced again to carbonic oxide, and thus utilise it profitably. This could, for instance, be useful if one had a Martin furnace with relative gas-generators, near the high furnaces for turning pig-iron into steel.

The possibility of separating gaseous mixtures by means of centrifugal force, and this at a minimum cost, is another application of interest to all great metallurgical works. In fact, besides feeding the fuel with centrifugated and oxygenated air, to increase the smelting temperature, having to provide a certain quantity of CO at the top of the high-blast furnace, so as to obtain certain chemical reactions required for steel working, it would be more convenient to blow under the grate CO_2, derived by centrifugal force from the products of combustion emitted by the high furnace.

The result would be that the CO_2, passing through the strata of incandescent coal, would produce the following reaction, $CO_2 + C = 2CO$; there would thus be an excess of CO formed without the aid of atmospheric air, and therefore without being accompanied by nitrogen. The centrifugated and oxygenated air would then serve to transform the CO into CO_2, besides profiting by a partial re-utilisation of the C contained in the gaseous products of combustion.

In conclusion, we who have followed most attentively, almost from the beginning, the development and the practical affirmation of Signor Mazza's invention, feel convinced that we may assert that it is destined to have a great success in the industrial world, and, owing to the great variety of its applications, we believe that the adoption of the Separator will give economical results worthy of the greatest consideration.

Magnalium.—We have received samples of a new aluminium alloy "magnalium," which will be found useful for many purposes; it has a good silver-white colour, can be forged, and turned easily; the tensile strength is said to be equal to iron, and the electrical conductivity very little inferior to pure aluminium. There is doubtless a large field of usefulness for alloys of this description, and when their value is recognised by manufacturers, much of the apparatus that is now made in brass and gun-metal will be made in the lighter alloy. Magnalium can be obtained from the agent, J. Arthur Williams, 92, Hatton Garden, London, E.C.

THE PRESENT POSITION OF THE THEORY OF ELECTROLYSIS.*

By W. C. DAMPIER WHETHAM, F.R.S.

WHEN, early in the Nineteenth Century, the attention of physicists and chemists was directed to the newly-discovered phenomena of electrolysis, an explanation had immediately to be found for the striking fact that the products of decomposition appeared at the electrodes only, while the body of the solution was unaltered. It was seen that a continual passage of the opposite constituents of the electrolyte in opposite directions through the liquid must be going on, and the chain hypothesis of Grotthus was long accepted as a true picture of the means by which that passage occurred.

About 1830, Faraday, by accurate quantitative measurement, threw new light on the subject, and proved that a definite electric transfer always accompanied a given amount of chemical decomposition. The process of electrolysis now appeared as a kind of convection—a stream of positively electrified cations drifting in one direction, and a stream of negatively electrified anions drifting in the other, under the influence of the electromotive force.

The next step was made in 1853 by Hittorf, who directed attention to the unequal dilution of the solution round the two electrodes, and showed that it could be explained either by the existence of complex ions, by means of which unaltered salt or solvent was dragged to one or other electrode, or by an unequal velocity of movement of the opposite ions. If in any given case we assume or can prove that no complex ions exist, we can calculate the ratio between the velocities of the cation and the anion, for this ratio will be the same as that between the amounts of salt lost by the solution from the neighbourhoods of the anode and the cathode.

In order to determine the absolute velocities with which the two ions move under a given force, it was necessary to discover another relation between those velocities. This was done by Kohlrausch, who pointed out that, on the convective idea of electrolysis, the total electric transfer per second through the solution or the current must be equal to the product of the number of ions, the charge on each of them, and the velocity with which they move relatively to each other—that is, the sum of their opposite absolute velocities. Now, Kohlrausch had already described a satisfactory method of measuring the electric resistance of electrolytes by the use of alternating currents and a telephone, and had shown that, when the reverse electromotive forces at the electrodes were eliminated, the conduction of the current conformed to Ohm's law. The current through the solution would therefore be equal to the product of the conductivity and the potential gradient, and thus a relation was deduced between the molecular conductivity and the sum of the opposite ionic velocities under unit potential gradient —quantities which are known as the ionic mobilities. Combining these results with Hittorf's migration numbers, the absolute values of the ionic mobilities were obtained. Kohlrausch calculated many such mobilities, and showed that, in general, they increased with the dilution of the solution. When several salts containing a common ion, as, for instance, the chlorides of the three metals potassium, sodium, and lithium, were examined, it was found that the values of the mobilities of the common ion chlorine, which differed in the three salts at moderate concentrations, approached each other as the dilution increased, and became identical at a dilution of about 100 litres per grm. equivalent of dissolved salt. To such a monovalent ion as chlorine, then, can be assigned a definite specific ionic mobility, which, at great dilution, is independent of the nature of the other ion present.

The first direct experimental confirmation of Kohlrausch's theory was given by Lodge, who measured the velocity with which hydrogen ions travelled along a tube filled with a jelly solution of a salt which contained an indicator, showing the presence of acid by a change of colour. Further experiments were made by the present writer, who traced the movement of the boundary between two solutions which were themselves of different colours. When the colour difference is due to the cations, the colour boundary travels with the current; when it is due to the anions, it moves against the current. This method has lately been improved and extended by Orme Masson and Steele. The general results confirm Kohlrausch's theory; the observed velocities agree with those calculated, and a very close coincidence is found throughout a considerable range of concentration for salts of monovalent ions. For divalent salts, slight discrepancies appear at higher concentrations, indicating the existence of complex ions; in this confirming the results of other lines of research.

The result of the investigations we have described clearly establishes the convective view of electrolysis; opposite streams of ions certainly pass through the solution, with the velocities indicated by Kohlrausch's theory, carrying their electric charges with them. To allow this migration a certain freedom of movement is necessary; how this freedom is secured is another question.

There is evidence to show that the migratory freedom is not produced as an effect of the electric forces, but exists whether or not such forces act. When the reverse polarisation at the electrodes is eliminated by the use of alternating currents or otherwise, it is well known that the conduction of electricity through solutions conforms to Ohm's law. The current is directly proportional to the electromotive force, and any force, however small, will consequently produce a corresponding current. In the body of the liquid, then, there can be no appreciable reverse electromotive forces, and no chemical or other reversible work is done when a current passes, all such work being located at the electrodes. Thus it follows that the current does no work in giving the ions the independence required for their electrolytic functions; the part played by the electromotive force is merely directive, and the only work expended by it goes in moving the ions, which already possess the necessary freedom, against the frictional forces of the viscous medium.

So far our argument shows that under all conditions the ions of a conducting solution possess the freedom which allows their passage through the liquid under the action of an electromotive force, but we have not considered the essential nature of this migratory freedom. Two alternatives seem to present themselves. Either the ions may migrate independently of each other, in accordance with the dissociation hypothesis, or else they may work their way through the solution by taking advantage of the successive formation and decomposition of molecular aggregates, or of collisions between the dissolved molecules, and the consequent possibility of ionic interchanges, in some such manner as is pictured in Grotthus's chain.

Let us assume for the moment the latter hypothesis, and trace the consequences. The solute molecules are scattered throughout a large volume of solvent, and, on this view, the ions work their way along from molecule to molecule of the solute, at the instants of collision between those molecules. Their velocities must therefore depend in some way on the frequency of collision, and this frequency, we learn from the kinetic theory, varies as the square of the concentration of the dissolved molecules. The ionic mobilities then will increase with the concentration, probably approximately as its square, while the conductivity, which, on the convective idea, is proportional to the product of the mobility and the concentration, will vary more or less proportionally to the cube of the concentration. These consequences of the hypothesis are contrary to observation, which shows that in general the ionic mobilities only vary slowly with dilution, usually slightly falling as the concentration increases, while the conductivity of a dilute solution is directly proportional to the first power of the concentration instead of to its cube, and increases more slowly than the concentration as the solution becomes stronger.

* A Paper read before the Faraday Society, June 30, 1903.

The view which refers the ionic mobilities to molecular interchanges, is thus clearly untenable, and we are driven to examine further the hypothesis of ionic dissociation. Here may be emphasised the point that the dissociation indicated by the electrical properties of solutions is merely a dissociation of the ions from each other, and does not require the supposition that they are free from all chemical combination; forces would certainly exist between the ions and the solvent, and there seems no reason to assume that chemical union between them cannot occur. Molecular complexes with an ion for a nucleus may exist, definite compounds may be formed, or some kind of double decomposition result in the production of new molecules, in which an ion retains its electric charge. About these various possibilities the electrical evidence has nothing to say, an effective migratory independence from each other is all that the ions need to produce the observed phenomena.

The dissociation theory, reached by the arguments outlined above, is supported, and was indeed originally suggested, by other relations. The possibility of assigning specific ionic mobilities, which are independent of the other ion present, is strong evidence for mutual ionic independence. The additive nature of the properties of electrolytes —their colours, for example—though perhaps too much stress has sometimes been laid on it, still tells the same tale. These and other similar arguments are familiar to all readers of text-books on the subject, and need not here be considered in detail. Evidence less well known is given by the power possessed by electrolytes of coagulating certain colloidal solutions, such as those of the sulphides of arsenic and antimony. It has been found by Schulze, by Linder and Picton, and by Hardy (Schulze, *Journ. Prakt. Chem.*, 1882, xxv., 431; Linder and Picton, *Journ. Chem. Soc. Trans.*, 1895, lxvii., 63; Hardy, *Journ. Physiol.*), that this coagulative power stands in a remarkable relation to the valency of the reacting electrolyte, the relative effects for salts with monovalent, divalent, and trivalent ions being represented by the ratios $1 : 30$ or $40 : 1000$ or 1600. Such results are explicable on the view that the modification of conditions which results in coagulation is produced by the action on a colloid particle of a certain minimum electric charge (Whetham, *Phil. Mag.*, 1899, 5, xlviii, 474; also Hardy and Whetham, *Journ. Physiol.*, 1899, xxiv., 288). An equal charge is brought up by the conjunction of two triads, three diads, or six monads, and, by the principles of the kinetic theory; this relation leads to the values for the ratios of the coagulative powers of $1 : x : x^2$. Putting x equal to 30 or 40, we get, within the limits of experimental error, an exact concordance with the observed results. This explanation has lately been supported by an experiment of Hardy, who finds that the less penetrating rays from radium, which consist of positively charged particles, comparable in size with the hydrogen atom, are likewise able to induce coagulation in solutions of proteid (*Journ. Physiol.*, xxix.; Appendix, p. xxix.).

Thus, taken together, the electrical properties of aqueous solutions yield an overwhelming amount of evidence in favour of the migratory independence from each other of the ions of the dissolved substances. The same conclusion has been reached by an entirely different method of research.

The theory of osmotics rests on a thermodynamic basis, from which we may approach it in two ways. We may accept the pressure-solubility relations of gases, and deduce the results by a thermodynamic cycle in a cylinder with semi-permeable diaphragms, in the original manner of van 't Hoff (*Phil. Mag.*, 1888, 5, xxvi., 88), which has been followed by Lord Rayleigh (*Nature*, 1897, lv., 253), or we may with Willard Gibbs, von Helmholtz, and Larmor (Gibbs, *Trans. Connect. Acad.*, 1875, iii., 138; von Helmholtz, *Abhandlungen*, 1883, iii., 101; Larmor, *Proc. Cambridge Philos. Soc.*, 1897, ix., 240; *Phil. Trans. A.*, 1897, cxc., 205), treat the subject from the fundamental ideas of the molecular theory. By the latter method we must regard the solute as distributed throughout the solvent as a number of discrete particles, each of which may effect, either by way of chemical combination or physical influence, a certain minute volume of the solven lying round it. The nature of this influence is unknown but, whatever it may be, as soon as the solution becomes so dilute that, except for an inappreciable fraction of the time, these spheres of influence do not in general intersect each other, any further addition of solvent will only increase the separation of these spheres of action; it cannot change the internal condition of one of them, tha is, it cannot affect the interaction between the solute particles and their surrounding solvent. The change of available energy produced by the entry of solvent, must then simply be that due to the dilution of the solute particles, and cannot depend on any interaction between solute and solvent. Now the osmotic pressure which a solution will exert against a solvent is measured by the rate of change of the available energy of the system when solvent is allowed to enter the solution reversibly through a semi-permeable membrane. The osmotic pressure then must, from what we have said above, be independent of the nature of the solvent, and will, therefore, have the same value if no solvent be present. Thus, in cases where this is possible, that is for volatile solutes, it follows that the osmotic pressure must be equal to the gaseous pressure corresponding to the same concentration. In this way we establish, theoretically, the gaseous laws for the osmotic pressure of volatile solutes, and, since volatility is probably only a matter of degree, it seems reasonable to extend this result to non-volatile bodies. Whether this extension be regarded as theoretically valid or not, there is abundant experimental evidence that it is practically justified, since the osmotic pressure of such substances as cane-sugar is well known to have the gaseous value.

(To be continued).

REPORT ON THE SEPARATION OF NITROGENOUS BODIES.*

By L. L. VAN SLYKE.

The referee decided to confine his work this year to the proteolytic products of milk and cheese in the hope of preparing methods of estimation which could be later subjected to critical examination at the hands of different analysts. The work covered by this report has been largely done in the laboratory of the New York Agricultural Experiment Station, at Geneva, by Mr. E. B. Hart. This report is more accurately entitled "Methods for the Estimation of the Proteolytic Compounds contained in Cheese and Milk."

When milk-casein and its salts, or paracasein in cheese and its salts, are acted upon by dilute acids or alkalis under certain conditions, or by enzymes, or by micro-organisms, the proteid bodies are split up, forming a variety of complex cleavage products. The extent and intensity of such proteolytic changes are measured by the proportions and kinds of the different compounds resulting from the decomposition. In the ripening process that takes place in cheese, we have an instance of extensive proteolysis in the case of the nitrogen compounds of the fresh cheese, due probably to the combined action of dilute acid, enzymes, and micro-organisms. In our study of the causes that produce cheese-ripening and of the conditions that influence the process, we were, at the start, brought face to face with the difficulty involved in the lack of satisfactory methods for making quantitative separations and determinations of the products of cleavage formed. While we have well-elaborated methods for estimating the amount of casein and albumin in fresh milk, these are of little aid in studying the products of their decomposition. Little attention has been given to the development of methods that are applicable to the products occurring in this field. Serious difficulties are in-

* Proceedings of the Nineteenth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, D.C.

volved in such a study. First, we know at present only in an extremely meagre and vague way the chemical constitution of milk-casein and its allied compounds. As regards the constitution of the various compounds formed by the proteolysis of casein, we are largely in the dark, except in the case of some of the simpler ones. In the second place, this field is difficult to study, because the quantities of individual compounds that we have to work with are usually very small. Under these conditions, methods of quantitative separation must, at best, be regarded as largely empirical, and more or less tentative. Instead of estimating individual compounds, about which our chemical knowledge is complete, we are compelled, in a large degree, to estimate groups of compounds, the individual members of which we know, for the most part, incompletely or not at all.

From the peptic digestion of casein, Chittenden has separated the proto- and deutero-caseoses ("Studies in Physiol. Chem.," Yale Univ., 1884-85, ii., 156), and from a tryptic digestion, a deutero-caseose and a peptone ("Studies in Physiol. Chem.," Yale Univ., 1887-88, iii., 66), Alexander (*Zeit. f. Physiol. Chem.*, 1898, xxv., 411) has separated hetero-caseose from a peptic digestion of casein, but only in small quantities. Many investigators have observed paranuclein or pseudonuclein, the insoluble residue remaining from the peptic digestion of casein or paracasein. Emil Fischer and P. A. Lavene (*Zeit. f. Physiol. Chem.*, 1901, xxxiii., 170) have obtained pyrrolidin-α-carbonic acid from a tryptic digestion of casein.

By hydrolysis of casein with hydrochloric acid, Cohn (*Ber.*, 1896, xxix., 1785) obtained 1-parahydroxyphenyl-α-amidopropionic acid (tyrosin), 1-α-amido-isobutylacetic acid (leucin), amidosuccinic (aspartic) acid, α-amidoglutaric (glutamic) acid, a pyridine derivative, and ammonia; by the same means, Emil Fischer (*Zeit. f. Physiol. Chem.*, 1901, xxxiii., 151) has recently isolated, among the monoamido acids, in addition to products previously obtained by others, amidovaleric acid, phenyl-α-amidopropionic acid (phenylalanine), pyrrolidin-α-carbonic acid, and probably amido-acetic acid (glycocol).

Among the crystallisable end-products which have been found in ripening cheese are the following:—Tyrosin, leucin, histidin, α-ε-diamidocaproic acid (lysin), tetramethylenediamine (putrescin), pentamethylenediamine (cadaverin), lysatin, guanidine probably, and ammonia. Most of these products have been recently reported by Winterstein and Thöny (*Zeit. f. Physiol. Chem.*, 1902, xxxvi., 28) as being found in Emmenthaler cheese. Excepting cadaverin and guanidine, they had also been previously found, though not reported, in American cheddar cheese in this laboratory. It is very probable that other amido compounds will be found, sooner or later, among the products formed by the tryptic, if not the peptic, digestion of milk-casein and of cheddar cheese.

In cheese we find, earlier or later, during the ripening process, a series of compounds and groups of compounds, which, so far as we know at present, appear in something like the following order of succession:—(1) Paracasein, (2) unsaturated paracasein lactate, (3) paranuclein (pseudonuclein), (4) caseoses (albumoses), (5) peptones, (6) amido-acid compounds, and (7) ammonia. After the early stages of ripening we have present at the same time all these different compounds and groups.

We shall consider methods for the separation and estimation of the proteolytic products found, first in cheese, and second in milk, following the general order indicated above. It may be well to say at the outset that in dealing with the separation of nitrogeneous bodies so complex in composition as those mentioned above, and occurring in very variable quantities, we can hope at present in the study of milk and cheese problems only to approximate accurate quantitative results. While we have in the Nencki method a very accurate means of estimating ammonia, the methods used in separating peptones from amido compounds can not be relied upon to give us more than approximate results.

I. Methods for the Separation and Estimation of the Nitrogen Compounds of Cheese.

The description and discussion of the methods used for the separation and estimation of the nitrogen compounds of cheese will be presented in the following order:—

1. Obtaining sample.
2. Determination of total nitrogen in cheese.
3. Extraction of water-soluble products.
4. Determination of total water-soluble nitrogen.
5. Determination of nitrogen in the form of paranuclein.
6. Determination of nitrogen in the form of proteids coagulable by heat in neutral solution.
7. Determination of nitrogen in the form of caseoses (albumoses).
8. Determination of nitrogen in the form of amido-acid compounds.
9. Determination of nitrogen in the form of peptones.
10. Determination of nitrogen in the form of ammonia.
11. Determination of nitrogen in the form of unsaturated paracasein lactate.

1. *Obtaining Sample of Cheese.*

A sample of cheese is obtained for analysis by means of a cheese-trier, which enables one to secure a round plug of cheese about half an inch in diameter and four to six inches long. Four or five plugs are drawn, one within a short distance of the centre of the cheese, one about an inch from the outer circumference, and the others at points equidistant between the two previous ones taken. Samples thus taken represent practically all different conditions existing in the cheese. After each plug of cheese is removed, about an inch of the end having the rind is cut off, and the rest is placed in a well-stoppered, large-mouthed sample bottle. The end with the rind is dipped once or twice in melted paraffin, and then carefully replaced in the cheese, being pushed in a little below the surface. After all the plugs have been taken and the ends properly replaced in the cheese, some of the melted parraffin is poured over the surface to fill up and surround the depressions made by replacing the ends of the plugs. This treatment generally ensures the exclusion of moulds, and prevents abnormal loss of moisture in the portions of cheese near the holes left by the removal of the cheese-plugs. This is a matter of much importance, when one intends to keep the same cheese for one or two years for systematic examination.

When all the plugs of cheese needed have been taken, the analysis should not be long delayed. The cheese in the bottle is cut into small pieces with a spatula, and stirred within the bottle, in order to mix the whole into as homogeneous a mass as possible.

2. *Determination of Total Nitrogen in Cheese.*

We weigh out 1 or 2 grms. of the cheese, prepared as described above, for the determination of total nitrogen, and treat it according to the Kjeldahl-Gunning method, modified as follows:—When the solution has become partially digested, we add a piece of copper sulphate about as large as an ordinary pea. Unless this is done, it will take a long time to convert the organic nitrogen completely into ammonia.

3. *Extraction of Water-soluble Products.*

In a porcelain mortar, we thoroughly mix 25 grms. of our cheese sample, prepared as indicated above, with about an equal bulk of clean quartz sand. This mixture is transferred to a 450 c.c. Erlenmeyer flask, to which we add about 100 c.c. of distilled water at a temperature of 50° C. The flask is then placed on a water-bath or in some place where it can be kept at a temperature of 50° to 55° C., and is allowed to stand for half-an-hour, being vigorously shaken from time to time. The liquid portion is then decanted through a filter of absorbent cotton into a 500 c.c. flask. The residue is again treated with 100 c.c. of water,

heated, agitated, and the liquid decanted as before. This process is repeated until the filtrate, after being cooled to room temperature, amounts to 500 c.c., exclusive of the fat, which usually is present at the top of the liquid.

The cotton filter mentioned is made of two layers of absorbent cotton prepared as follows :—In a glass funnel we place some absorbent cotton to the depth of about 1 inch ; moisten this with water, in order to compact it, and then above this place another layer of cotton of the same thickness. Upon this we pour our portions of cheese extract. This kind of filter allows rapid filtration without the aid of a pump, and is as effective in every way as paper, which requires half a day or more for complete filtration of 500 c.c. of extract. Several samples of cheese can be extracted at the same time. The upper layer of cotton holds all solid particles, and can be returned to the flask for extraction with salt solution.

The method of making a water extract of cheese, as described above, insures the complete removal of all water-soluble nitrogen compounds present in the cheese without danger of coagulating any soluble proteids. The use of water at room temperatures is not, in our experience, equally effective in making a complete extraction of the water-soluble products. Under some conditions, as in the early stages of ripening cheese at low temperatures, small amounts of a body are extracted by water which is precipitated by heat in neutral solution. We are unable to say at present whether this body consists of acid salts of paracasein or of hetero-caseose, which are practically insoluble in water, or whether it is some other compound. The temperature of 50° C. also has the advantage of arresting further peptic or tryptic action during the extraction. The use of acids in extracting cheese is to be avoided, since a small amount of acid will not only precipitate the soluble nuclein, but may form salts with paracasein, which are somewhat soluble in a slightly acid solution ; the amount of dissolved paracasein salts under such circumstances depends on the amount of acid used and the time of extraction.

4. *Determination of Total Water-soluble Nitrogen.*

For the determination of the amount of total water-soluble nitrogen, we take 50 c.c. of the water extract, prepared above, equivalent to 2·5 grms. of cheese, and treat it according to the Kjeldahl method for determing nitrogen.

5. *Determination of Nitrogen in the Form of Paranuclein (Pseudonuclein).*

To 100 c.c. of the water extract, equivalent to 5 grms. of cheese, we add 5 c.c. of a 1 per cent solution of hydrochloric acid, and warm the mixture on the water-bath at 50° to 55° C. until complete separation takes place, as shown by a clear supernatant liquid. The precipitate is filtered, washed with water, and then, with the filter-paper, treated by the Kjeldahl method to determine the amount of nitrogen. The nitrogen equals nitrogen present in the form of paranuclein (pseudonuclein).

In our early work 2 or 3 c.c. of a saturated alum solution were used for this determination, for the reason that in the separation of casein in milk we had used this reagent successfully ; but at the time the nature of the body we were precipitating from our water solution of cheese was not known. Later, when we had studied it and learned its character, it was found, on comparing precipitations, by use of alum and by hydrochloric acid, that alum gave high results, undoubtedly precipitating some caseoses. In 27 comparative trials with water extracts of different cheeses, we found in the alum precipitate nitrogen varying from 0·2 to 0·337 per cent of the cheese, and averaging 0·269 per cent, while the nitrogen in the hydrochloric acid precipitate varied from 0·046 to 0·145 per cent of the cheese, and averaged 0·085 per cent. The nitrogen precipitated by alum in these 27 cases was from 2·1 to 5·5 times as much as that precipitated by hydrochloric acid, the average of all being 3·2. Since hydrochloric acid is known to precipitate paranuclein completely, we are justified in assuming that the alum precipitates other compounds, and this is confirmed by other work, showing that when alum is used as the first precipitant we get smaller quantities of caseoses in the filtrate than we do when we use hydrochloric acid as the precipitant of paranuclein. Alum appears to resemble zinc sulphate as a precipitant of proteids.

Paranuclein (pseudonuclein) results from the breaking down of casein or paracasein, and is always found in the water extracts of ripening cheese, whether salted or unsalted. It may, perhaps, be regarded more accurately as a residue, and probably should not be counted as one of the products to be used in measuring the extent of cheese ripening. This is undoubtedly the same body as Chittenden's dyspeptone ("Studies in Physiol. Chem.," Yale University, 1887-88, iii., 66), which he found as an insoluble residue in a pepsin-hydrochloric-acid digestion of casein.

6. *Determination of Nitrogen in the Form of Proteids Coagulable by Heat in Neutral Solution.*

The filtrate from the preceding determination (5) is made neutral with dilute caustic potash, using phenolphthalein as an indicator. It is then heated at the temperature of boiling water, until any coagulum that forms settles completely, leaving a clear supernatant liquid. The precipitate is washed with water, and its nitrogen determined by the Kjeldahl method. In our experience, such a precipitate rarely occurs, except in the case of cheese ripened near freezing-point. The nature of this body we have not yet investigated.

7. *Determination of Nitrogen in the Form of Caseoses (Albumoses).*

The filtrate from the preceding determination (6) is treated with 1 c.c. of 50 per cent sulphuric acid, saturated with chemically pure zinc sulphate, and then warmed to about 70° C. until the caseoses separate completely and settle. The mixture is allowed to cool, and is then filtered. If filtered hot, there will occur a further separation of caseoses in the filtrate on cooling. The precipitate is washed with a saturated solution of zinc sulphate made slightly acid with sulphuric acid. The nitrogen in the precipitate is determined by the Kjeldahl method.

For the determination of caseoses, the use of ammonium sulphate was exclusively employed until Bömer (*Zeit. Analyt. Chem.*, 1895, v., 562) proposed the use of zinc sulphate, which possesses a distinct advantage in enabling one to determine nitrogen directly in the precipitate or filtrate. This method has been employed, in the estimation of caseoses, also by the Wisconsin Agricultural Experiment Station. In the present state of our knowledge of this class of compounds, zinc sulphate must be regarded as the most available reagent for their quantitative separation.

8. *Determination of Nitrogen in the Form of Amido-acid Compounds.*

The amido-acid compounds are determined in the filtrate from the precipitation of peptones (9). For the removal of peptones three reagents have been commonly used :—(1) Tannin and sodium chloride, (2) phosphotungstic acid with sulphuric acid, and (3) bromine with hydrochloric acid. After the removal of peptones the filtrate contains amido-acid and ammonia compounds. After determining the amount of total nitrogen in this filtrate, and then the amount of nitrogen present in the form of ammonia (as obtained in 10, see *prox.*), we subtract the amount of ammonia nitrogen from the combined amount of amido-acid and ammonia nitrogen, and thus obtain the amount of amido-acid nitrogen. In the following section (9) we describe the methods involved in removing peptones by the different reagents and the efficiency of each reagent.

(To be continued).

NOTICES OF BOOKS

Twenty-seventh Annual Report of His Majesty's Inspectors of Explosives; being their Annual Report for the Year 1902. London: Darling and Son, Ltd., and Eyre and Spottiswoode. Edinburgh: Oliver and Boyd. Dublin: E. Ponsonby. 1903. Pp. 234.

The only modification of the law made during the past year with regard to explosives, has been the order of the Secretary of State relative to the packing of chlorate mixtures.

Owing to the conclusion of the war in South Africa, the manufacture of explosives for the War Department has fallen away to comparatively small dimensions, but this has been counterbalanced by an increase in the demand for explosives for more useful purposes, so that the end of the war has been of advantage to the trade in general.

As the result of their visits of inspection to the various factories and magazines throughout the kingdom, the inspectors find no reason to complain that there is any falling off in their condition and management. A large portion of their time has been devoted as usual to visiting stores and registered premises throughout the kingdom; they regret to say, however, that though in some places these stores and registered premises are well looked after, in general the administration of the Explosives Act by local authorities leaves much to be desired. Their experience in this respect has led them to the conclusion that in the case of so highly technical an Act, decentralisation is undesirable.

The number of deaths (13) from accidents by fire or explosions, though not high, is above the average for the decade; it will, however, compare favourably with the death-rate in other dangerous trades.

The total number of factories under continuing certificate or licence is 150; of this total, four factories are under notice of temporary disuse. Four factories have become extinct during the year, and there have been five applications for licenses for new factories, and there were four outstanding from 1901, making nine in all. There have been sixteen new explosives added to the authorised list and four removed from it, with five alterations in definition.

It will be seen from Dr. Dupré's report, Table I., that out of 406 samples examined by him, 36 were rejected; 3 samples of blasting gelatin were rejected out of a total of 43; 12 samples out of 28 of carbonite; none out of 14 of dynamite; none out of 51 of gelatin dynamite; 1 out of 113 of gelignite; and 1 out of 5 of saxonite.

During the year there were four prosecutions for illegal manufacture.

The amount of foreign blasting explosives containing nitroglycerin imported during 1902 is greater than in 1901, the figures being 1,839,277 lbs. against 1,473,950 lbs. The importations of blasting explosives not containing nitroglycerin shows a considerable falling off; the figures were for 1902, 12,000 lbs., and for 1901, 142,900 lbs.

In connection with their visits of inspection the Inspectors found it necessary to institute proceedings in two cases, being the same number as in 1901. Particulars of these cases are given in Appendix T (*a*). In addition to the above cases, proceedings have been taken by the local authorities in 6 cases on behalf of, or on information supplied by, the Inspectors.

It is to be regretted that the working of the Act by the local authorities is so unsatisfactory. Out of 103 places inspected during the year, the majority being towns, no less than 43 have been classed as "Indifferent" to "Very Bad"; and in these there may be said to be real danger to person and property from the neglect of those precautions in regard to the keeping of explosives which the Act enjoins. Specially noteworthy among these are the City of London, the City of Glasgow, the City of Manchester, and the Rugby division. It is satisfactory to read, however, that in the first three of the above cases, the local authorities have taken steps to put matters on a more satisfactory basis. In most instances the cause of this unsatisfactory state of things is simply apathy on the part of the local authority and its officer; there are, however, other causes which militate against the efficient administration of the Act. One of these is the frequent changing of the officers appointed by the local authorities, and the consequent difficulty these officers have in acquiring a thorough knowledge of their duties.

Chemical and Pharmaceutical Industries. ("Les Industries Chimiques et Pharmaceutiques"). By Albin Haller, Membre de l'Institut. In Two Volumes. With 108 Figures. Paris: Gauthier-Villars. 1903. Pp. 405 and 445.

These two volumes form the report of the Chemical Jury of the International Exhibition of 1900, and deal with the whole subject in a most thorough and comprehensive manner.

As with other exhibits, those of chemical and pharmaceutical products were more particularly exhibits of manufactured articles, but while recognising the inherent difficulties attending a rigorous classification of materials so various as those forming the subject of this work, the author has formed them into chapters, among the principal of which we may mention those on "Artificial Colouring Materials and Extracts of Dye-woods"; "Products of Dry Distillation—Petroleum"; "Natural and Synthetic Perfumes"; "Mineral Colours, Lakes, and Varnishes"; "Soaps"; "Artificial Silks"; and "Colonial Products."

Each chapter deals in a general manner with the special industry which is described therein, its development, and the modifications it may have undergone during the last ten years. Then follows a list of the principal exhibitors in that particular class, with details of their exhibits. Finally, the most important discoveries or improvements in each particular line are summarised.

There is a short index at the end of each volume.

Subject-list of Works on Architecture and Building Construction, in the Library of the Patent Office. Bibliographical Series, No. 9. London: Darling and Son, Ltd. 1903. Pp. 164.

Like those that have preceded it, this subject-list consists of two parts:—(*a*) A general alphabet of subject headings, with entries in chronological order of the works arranged under these headings; (*b*) a key, or summary of these headings shown in class order.

The present list comprises 1344 works (71 serials, 1273 text-books, &c.), representing some 3173 volumes. The catalogue entries relating to these works number 1739, and are distributed under 217 headings and sub-headings.

Analysis, Detection, and Commercial Value of the Rare Metals. By Dr. J. Ohly, Ph.D. Industrial Printing and Publishing Company, Denver, Colorado, U.S.A.

This small treatise will be found of considerable value to those engaged in work upon the rare metals. It contains in small compass much useful information difficult to collect from other sources. Each of the rare metals is treated under six heads:—History, Chemistry, Mineralogy, Detection, Qualitative and Quantitative Estimation. The historical accounts are particularly interesting, and have been introduced to stimulate research by showing the manner in which the difficulties encountered in the discovery and isolation of the various elements have been overcome. In dealing with the mineralogical data, the occurrence of rare minerals in America has been developed more fully than in the case of foreign localities. A good deal of attention has been given to the now very important uranium ores (the source of radium), both in the body of the work and in the appendix; this latter contains some useful matter not strictly connected with rare metals; for instance, the estimation of sulphur in coal, the electric furnace, and the analysis of crude pretoleum.

Unfortunately there is no index, and one has to be content with a very meagre "table of contents," but for all that the work will be found of value to assayers, chemists, and prospectors, for whose special benefit it has been compiled.

CORRESPONDENCE.

THE SCINTILLATIONS OF RADIUM.

To the Editor of the Chemical News.

Sir,—Having removed the pointer with the speck of radium nitrate from my Spinthariscope with the object of testing some minerals for radio-activity, I looked into the apparatus first to ascertain that all was dark, but was surprised at seeing, not only several large motionless stars (which I suppose may be due to radium nitrate deposited when the pointer dropped on to the screen whilst removing it), but a considerable number of bright scintillations—brighter and larger than those in the "luminous sea" seen when the pointer is present. If not troubling you too much, will you kindly say whether you have observed this, and what explanation can be given?—I am, &c.,

C. S. Stanford Webster.

[The phenomena have been already described. See Chemical News for April 3, 1903.—*Ed.* C. N.].

CHEMICAL NOTICES FROM FOREIGN SOURCES

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 2, July 13, 1903.

Combination of Ferric Sulphate with Sulphuric Acid.—A. Recoura.—Ferric sulphate combines very easily with sulphuric acid, giving rise to an acid containing one molecule of ferric sulphate and one molecule of sulphuric acid, which the author calls ferrisulphuric acid. This acid is a light white powder which is very soluble in water, giving a pale yellow solution. Analysis shows it to have the formula $Fe_2O_34SO_39H_2O$.

Action of Carbon Monoxide on Iron and its Oxides.—Georges Charpy.—The action of carbon monoxide on iron and its oxides is important, on account of its relation to metallurgical reactions. When sesquioxide of iron is heated in a continuous current of carbon monoxide, the complete reduction of the oxide takes place, and metallic iron—more or less carburetted—is left. The reaction takes place at all temperatures between 200° and 1200°, but is naturally more rapid at the higher temperatures.

So-called Colloidal Silver.—M. Hanriot.—The so-called colloidal silvers which the author examines have definite chemical composition and properties. It is proved that the albumenoid matter in collargol and the silver in silvercargol do not constitute impurities, but form an integral portion of the molecule, not only because it is apparently impossible to separate the constituents without destroying the colloidal silver, but also because these bodies have lost their reactions and habitual solubilities. All colloidal silvers when heated in a vacuum evolve carbon dioxide and hydrogen, and have a greater reducing power than that of the silver they contain.

Action of Hypophosphorous Acid on Diethylketone and Acetophenone.—C. Marie.—When hypophosphorous acid acts on diethylketone aad acetophenone, the acids $PO_2H_3(C_2H_5)CO(C_2H_5)$ and $PO_2H_3(CH_3)CO(C_6H_5)$ are produced. The existence of these two acids, when compared to those of the acids prepared by means of PO_2H_3 and the other ketones, whether symmetric or non-symmetric, fatty, or aromatic, show that the reaction by which they are formed is a general one, and is the same as the oxidation reaction which gives the corresponding oxyphosphinic acids.

Phenylpropargylidene Chloride, $C_6H_5-C\equiv C-CHCl_2$.—Ernest Charon and Edgar Dugoujon.—With the exception of the isomeric transformations of hydrocarbons, the preparation of phenylpropargylidene chloride affords the first example of the action of the triple liaison on the hydrocarbon group, and on the chlorated substitutions in this group. The authors believe that, in the case of chlorated substitution, the triple liaison is less accentuated than that of the double liaison.

Preparation of Secondary Amides.—J. Tarbouriech.—By making the acid chlorides of a number of carbon atoms differing from those of the primary amides, the author obtains mixed or disymmetric amides—a series of which no member, up to the present time, has been prepared. He successfully prepares the following members of the series:—Normal dibutyramide, di-isobutyramide, di-isovaleramide, and normal divaleramide.

Action of Ammonium Persulphate on Metallic Oxides.—A. Seyewetz and P. Trawitz.—When ammonium persulphate acts on metallic oxides reactions take place, which differ considerably from those taking place with hydrogen peroxide. With protoxides a displacement of the ammonia takes place with a probable formation of the corresponding persulphate, or the production of sesquioxides or peroxides. This latter reaction is particularly interesting in the preparation of precipitated lead peroxide. With the sesquioxides or peroxides, it is possible either to produce oxidation of a portion of the ammonia by evolving nitrogen at the same time as the sulphate corresponding to the oxide is produced, or the formation of the oxide with evolution of the oxygen from a portion of the persulphate; or, finally, complete peroxidations, as those obtained with chromium and manganese hydrates.

Action of Bromine on Pinene in presence of Water.—P. Genvresse and P. Faivre.—The action of bromine on pinene has been the object of many researches, and many contradictory results have been arrived at. The authors re-investigate this reaction by another method. They operate in presence of water, care being taken that the temperature is kept low. The oil obtained is retained by the water vapour. A colourless liquid is first produced lighter than water, which consists chiefly of unaltered pinene; after this a yellow oil heavier than water is obtained from which cymene can be extracted, and, finally, a liquid which crystallises. There remains in the apparatus a viscous brown residue. The crystals so obtained melt at 167—168° after crystallisation from acetic ether. They form a saturated compound, and analysis shows them to have the formula $C_{10}H_{16}Br_2$ (pinene dibromide). M. Wallach obtained these by another method. The formation of this substance is of great importance because it shows the divalence of pinene.

MISCELLANEOUS.

City and Guilds of London Institute.—At a meeting of the Council of the City and Guilds of London Institute held July 30th the diploma of "Associate of the City and Guilds Institute" was awarded to the following matriculated third year students of the Central Technical College who have completed a full course of instruction as prescribed by the Council:—

Civil and Mechanical Engineering.—J. D. Griffin, R. C. Munro (Siemens Medal), H. H. Baxter, H. F. Bayley, W. E. G. Bender, G. W. M. Borns, C. E. Capito, J. R. Fox, E. A. Gatehouse, C. J. Gutmann, V. B. Harley-Mason, W. H. Hingston, E. W. Lace, E. Latham, E. de Lautour, R. E. Lehuraux, F. E. Maynard, J. E. M. McGregor, H. W. Nicholson, T. C. Ormiston-Chant, D. A. S. Porteous, L. F. Rampal, M. K. Rice-Oxley, F. . Salberg, E. A. Salt, C. F. Satow, A. E. Scoones, J. H

Segrave, C. G. Smith, V. C. Smith, C. E. Thomson, T. W. Wallace.

Electrical Engineering.—A. A. Gomme (Siemens Medal and Premium), J. M. de Artola, W. A. Burton, W. G. H. Cam, F. Creedy, R. S. Dahl, A. G. Ellis, E. P. Elwin, S. F. W. Finnis, A. L. Glegg, C. E. Greenslade, G. R. Griffin, P. H. Harding, M. S. Kennedy, A. H. Knight, T. F. Lee, L. Lehuraux, H. M. Lyons, F. Neuhaus, C. Petersen, H. S. Plymen, R. H. Turrall, L. D. Wainwright.

Chemistry.—E. F. Armstrong, R. J. Caldwell, J. V. J. Hayman, C. D. McCourt, F. J. Salmon.

In addition to the above, Certificates have been awarded to 26 matriculated third year students who have completed a full course of instruction at the Central Technical College, and to 55 students who have completed a full course of instruction at the Technical College, Finsbury.

Precipitation of Gold in the Crystalline Form, by means of Formic Aldehyde.—N. Averkief.—A solution of chloride of gold, strongly acidulated with hydrochloric or nitric acid, is precipitated on the addition of formic aldehyde. At the ordinary temperature the reaction is slow, and requires several days; if heated on the water-bath, a few hours is sufficient. The crystals are visible to the naked eye; their form is very definite; as a rule they are combinations of the cube and the octahedron. Rhombohedral dodecahedra, trapezohedra, and solids with forty-eight faces are also found. Their elements can be distinguished very easily with a magnification of 100 or 200 diameters. The length of the crystals deposited in the cold is about 0·9 m.m.; that of the crystals deposited under the influence of heat is less. For 200 or 300 c.c. of solution of chloride of gold containing 0·01 grm. of gold per litre, we use 10 c.c. of the ordinary solution of formic aldehyde. Gold can also be precipitated in the crystalline form, in the presence of ferrous or ferric salts, of salts of copper, antimony, mercury, zinc, lead, manganese, tin, arsenic, and of the metals of the first and second groups; the solutions must be strongly acid, as in a neutral or slightly acid solution containing iron the latter is precipitated in the form of a fine powder, having a crystalline structure. The density of the crystalline gold, precipitated by formic aldehyde, was found to be 19·4278 and 19·4341; mean, 19·43095. Platinum also is precipitated in the crystalline form under the same conditions, but more slowly than gold, especially in dilute solutions.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 828.

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THE CHEMICAL NEWS.

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RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

Introduction.

The object of the present work is the publication of researches which I have been carrying on for more than four years on radio-active bodies. I began these researches by a study of the phosphorescence of uranium, discovered by M. Becquerel. The results to which I was led by this work promised to afford so interesting a field that M. Curie put aside the work on which he was engaged, and joined me, our object being the extraction of new radio-active substances and the further study of their properties.

Since the commencement of our research we thought it well to hand over specimens of the substances, discovered and prepared by ourselves, to certain physicists, in the first place to M. Becquerel, to whom is due the discovery of the uranium rays. In this way we ourselves facilitated the research by others besides ourselves on the new radio-active bodies. At the termination of our first publications, M. Giesel, in Germany, also began to prepare these substances, and passed on specimens of them to several German scientists. Finally, these substances were placed on sale in France and Germany, and the subject growing in importance gave rise to a scientific movement, such that numerous memoirs have appeared, and are constantly appearing on radio-active bodies, principally abroad. The results of the various French and foreign researches are necessarily confused, as is the case with all new subjects in course of investigation, the aspect of the question becoming modified from day to day.

From the chemical point of view, however, one point is definitely established:—*i.e.*, the existence of a new element, strongly radio-active, viz., radium. The preparation of the pure chloride of radium and the determination of the atomic weight of radium form the chief part of my own work. Whilst this work adds to the elements actually known with certainty a new element with very curious properties, a new method of chemical research is at the same time established and justified. This method, based on the consideration of radio-activity as an atomic property of matter, is just that which enabled M. Curie and myself to discover the existence of radium.

If, from the chemical point of view, the question that we undertook primarily may be looked upon as solved, the study of the physical properties of the radio-active bodies is in full evolution. Certain important points have been established, but a large number of the conclusions are still of a provisional character. This is not surprising when we consider the complexity of the phenomena due to radio-activity, and the differences existing between the various radio-active substances. The researches of physicists on these substances constantly meet and overlap. Whilst endeavouring to keep strictly to the limits of this work and to publish my individual research only, I have been obliged at the same time to mention results of other researches, the knowledge of which is indispensable.

I desired, moreover, to make this work an inclusive survey of the actual position of the question.

I indicate at the end the particular questions with which I am specially concerned, and those which I investigated in conjunction with M. Curie.

I carried on the work in the laboratories of the School of Physics and Chemistry in Paris with the permission of Schützenberger, late Director of the School, and M. Lauth, actual Director. I take this opportunity of expressing my gratitude for the kind hospitality received in this school.

* Thesis presented to the Faculté des Sciences de Paris.

Historical.

The discovery of the phenomena of radio-activity is connected with researches followed, since the discovery of the Röntgen rays, upon the photographic effects of phosphorescent and fluorescent substances.

The first tubes for producing Röntgen rays were without the metallic anti-cathode. The source of the Röntgen rays was the glass surface impinged upon by the cathode rays; this surface was at the same time actively fluorescent. The question then was whether the emission of Röntgen rays necessarily accompanied the production of fluorescence, whatever might be the cause of the latter. This idea was first enunciated by M. Henri Poincaré.

Shortly afterwards, M. Henry announced that he had obtained photographic impressions through black paper by means of phosphorescent zinc sulphide. M. Niewenglowski obtained the same phenomenon with calcium sulphide exposed to the light. Finally, M. Troost obtained strong photographic impressions with zinc sulphide artificially phosphorescent acting across black paper and thick cardboard.

The experiences just cited have not been reproduced, in spite of numerous attempts to this end. It cannot therefore be considered as proved that zinc sulphide and calcium sulphide are capable of emitting, under the action of light, invisible rays which traverse black paper and act on photographic plates.

M. Becquerel has made similar experiments on the salts of uranium, some of which are fluorescent.

He obtained photographic impressions through black paper with the double sulphate of uranium and potassium.

M. Becquerel at first believed that this salt, which is fluorescent, behaved like the sulphides of zinc and calcium in the experiments of MM. Henry, Niewenglowski, and Troost. But the conclusion of his experiments showed that the phenomenon observed was in no way related to the fluorescence. It is not necessary that the salt should be fluorescent; further, uranium and all its compounds, fluorescent or not, act in the same manner, and metallic uranium is the most active. M. Becquerel finally found that by placing uranium compounds in complete darkness, they continue acting on photographic plates through black paper for years. M. Becquerel allows that uranium and its compounds emit peculiar rays—uranium rays. He proved that these rays can penetrate thin metallic screens, and that they discharge electrified bodies. He also made experiments from which he concluded that uranium rays undergo reflection, refraction, and polarisation.

The work of other physicists (Elster and Geitel, Lord Kelvin, Schmidt, Rutherford, Beattie, and Smoluchowski) confirms and extends the results of the researches of M. Becquerel, with the exception of those relating to the reflection, refraction, and polarisation of uranium rays, which in this respect behave like Röntgen rays, as has been recognised first by Mr. Rutherford and then by M. Becquerel himself.

Chapter I.

Radio-activity of Uranium and Thorium. Radio-active Minerals.

Becquerel Rays.—The uranium rays discovered by M. Becquerel act upon photographic plates screened from the light; they can penetrate all solid, liquid, and gaseous substances, provided that the thickness is sufficiently reduced; in passing through a gas, they cause it to become a feeble conductor of electricity.

These properties of the uranium compounds are not due to any known cause. The radiation seems to be spontaneous; it loses nothing in intensity, even on keeping the compounds in complete darkness for several years; hence there is no question of the phosphorescence being specially produced by light.

The spontaneity and persistence of the uranium radiation appear as a quite unique physical phenomenon. M. Becquerel kept a piece of uranium for several years in the dark, and he has affirmed that at the end of this time the

action upon a photographic plate had not sensibly altered. MM. Elster and Geitel made a similar experiment, and also found the action to remain constant.

I measured the intensity of radiation of uranium by the effect of this radiation on the conductivity of air. The method of measurement will be explained later. I also obtained figures which prove the persistence of radiation within the limits of accuracy of the experiments.

For these measurements a metallic plate was used covered with a layer of powdered uranium; this plate was not otherwise kept in the dark; this precaution, according to the experimenters already quoted, being of no importance. The number of measurements taken with this plate is very great, and they actually extend over a period of five years.

Some researches were conducted to discover whether other substances were capable of acting similarly to the uranium compounds. M. Schmidt was the first to publish that thorium and its compounds possess exactly the same property. A similar research, made contemporaneously, gave me the same result. I published this not knowing at the time of Schmidt's publication.

We shall say that uranium, thorium, and their compounds emit *Becquerel rays*. I have called *radio-active* those substances which generate emissions of this nature. This name has since been adopted generally.

In their photographic and electric effects, the Becquerel rays approximate to the Röntgen rays. They also, like the latter, possess the faculty of penetrating all matter. But their capacity for penetration is very different; the rays of uranium and of thorium are arrested by some millimetres of solid matter, and cannot traverse in air a distance greater than a few centimetres; this at least is the case for the greater part of the radiation.

The researches of different physicists, and primarily of Mr. Rutherford, have shown that the Becquerel rays undergo neither regular reflection, nor refraction, nor polarisation.

The feeble penetrating power of uranium and thorium rays would point to their similarity to the secondary rays produced by the Röntgen rays, and which have been investigated by M. Sagnac, rather than to the Röntgen rays themselves.

For the rest, the Becquerel rays might be classified as cathode rays propagated in the air. It is now known that these different analogies are all legitimate.

(To be continued).

THE PRESENT POSITION OF THE THEORY OF ELECTROLYSIS.*

By W. C. DAMPIER WHETHAM, F.R.S.

(Concluded from p. 79).

THE direct measurement of osmotic pressure is a matter of considerable difficulty, but there exists a theoretical connection between that pressure and certain other properties of the solution, such as the lowering of its vapour pressure and the depression of its freezing-point below the corresponding values for the pure solvent. Observations on the boiling- or freezing-points of solutions, then, enable the osmotic pressures to be calculated. As is well known, direct osmotic determinations, as well as the results of experiments on these correlated properties, yield abnormally great values in the cases of aqueous solutions of electrolytes. It was van 't Hoff's investigation of this phenomenon that originally suggested the idea of ionic dissociation to Planck and Arrhenius. Since the thermodynamic theory shows that the osmotic pressure of dilute systems depends only on the number and not on the nature of the dissolved particles or on the nature of the solvent, when the osmotic properties have abnormally great values for dilute solutions, it must follow that the number of dissolved particles is greater than that calculated from the chemical formula weight; that is, that dissociation must have occurred. It does not necessarily follow that the dissociation is that with which we have to deal when examining the electrical properties; whether it is or is not, is a matter for further inquiry. Complicated molecules, dissolved in non-aqueous solvents at any rate, seem sometimes to undergo dissociation into parts which are not electrical ions, for Kahlenberg has lately found that solutions of diphenylamine in methyl cyanide show abnormally low molecular weights, and yet are non-conductors of electricity (*Journ. of Phys. Chem.*, 1901, v., 344; 1902, vi., 48). On the other hand, it is difficult to see how more than one kind of dissociation is possible in such a molecule as potassium chloride, which we have already seen is dissociated into electric ions when dissolved in water.

In cases where the dissociation indicated by the osmotic pressure is found to be electrical in its nature, two separate relations have usually been held as necessary consequences of the dissociation theory. How far such suppositions are justified we will proceed to discuss.

The equivalent conductivity of a solution of a simple salt such as potassium chloride increases with dilution, and finally becomes constant. There seems reason to believe that the salt is then completely dissociated into its ions, which, in this case, are shown by the chemical and electrical properties to be two in number. If the osmotic phenomena are examined at dilutions corresponding to complete electrolytic dissociation, we ought to find indications here also that the molecule of potassium chloride behaves as though it were separated into two parts—the osmotic pressure and the freezing-point depression should possess double their normal values.

The only satisfactory measurements at the extreme dilutions necessary are those described by Mr. E. H. Griffiths to the British Association in 1901. The freezing-points of a solution of cane-sugar, as measured by the most accurate methods of platinum thermometry, were such that the molecular depression maintained a value of 1·858 from concentrations of 0·0005 to 0·02 normal. Taking 79·4 as the best value for the latent heat of fusion of water, the result, calculated thermodynamically from the gaseous value of the osmotic pressure, is 1·857. A solution of potassium chloride gave results which increased as the concentration diminished, finally reaching a value of 3·720 at a concentration of 0·0003 grm. equivalents per litre. Twice 1·857 is 3·714, agreeing, within very small limits of experimental error, with the observed result.

For no other electrolytes are such accurate cryoscopic data yet available. The observations of Loomis, which are put forward by Raoult in his recent work ("Cryoscopie," Paris, 1901) as in themselves trustworthy and in accordance with the best of the other known results, were carried only to concentration of 0·01 normal. At this concentration were found value for various binary electrolytes which approach the theoretical result within a few per cent. Substances which, like barium chloride or sulphuric acid, are shown by their electrical behaviour to produce three ions, gave a molecular depression of freezing-point some 10 per cent below the figure for complete dissociation, while salts with two divalent ions, such as magnesium sulphate, fail to reach 3·714 by about 30 per cent. In all these cases the discrepancies are in the direction suggested by the electrical conductivities, which, especially for the last class of salts, indicate that the dissociation is very far from complete at the concentration used in the cryoscopic experiments.

On the whole, then, the evidence is clearly in favour of the relation we are examining, in those cases which have been adequately examined at sufficiently great dilutions.

It has usually been considered that the dissociation theory required a further relation between the electrical and the osmotic measurements. At higher concentrations the equivalent conductivity diminishes, and this is held to denote incomplete ionisation. The actual value of the

* A Paper read before the Faraday Society, June 30, 1903.

equivalent conductivity, divided by its value at extreme dilution, is commonly taken as measuring the fractional coefficient of ionisation, which can obviously be also calculated from osmotic data on the assumption that each dissolved particle still causes the effect it would produce at infinite dilution. Many discrepancies between the values given by these two lines of research have been discovered, and it is necessary to examine how far the theory really suggests any coincidence.

The electrical value of the coefficient of dissociation assumes that no complex ions are present, and that the ionic viscosity of the solution is the same as that which the solvent offers to the passage of the ions at infinite dilution. It is probable that small errors are introduced by these assumptions, but on the other side much larger ones are possible. The deduction by the principles of thermodynamics of the gaseous value for the osmotic pressure is only valid for dilute systems—systems, that is to say, between the parts of which there are no appreciable forces. It is true for a gas at atmospheric pressure; it is true for a non-electrolyte at moderate dilution; but, as Dr. Larmor pointed out to the writer, we must not assume that inter-ionic forces will vanish at corresponding concentration.

In the light of our present knowledge, it is natural to represent a non-dissociated molecule as an electrical bipolar system. The forces between the widely separated molecules of the dissolved substance will be analogous to the translational forces between two small magnets at a distance from each other large compared with the length of either of them. Such forces vary inversely as the fourth power of the distance, and therefore become insensible as soon as that distance exceeds a very small value. Intermolecular effects, then, will vanish for the solute at moderate dilutions, and the osmotic properties conform to the gaseous laws.

On the other hand, representing an electrolyte in solution as chiefly composed of dissociated ions, we see at once that the forces between those ions are those between isolated particles, charged with opposite kinds of electricity. Such forces vary inversely as the square of the distance, and therefore remain effective at distances whereat the bipolar solute molecules have quite ceased to exert any mutual influence. Inter-ionic forces will thus produce disturbing effects even at very great dilution. The fact that the theoretical value for the freezing-point has been reached in the case of potassium chloride shows that, here at any rate, they vanish at a dilution which, though very great, is still experimentally attainable. It does not follow, however, that they remain insensible as the concentration rises, and the ionisation, determined electrically, ceases to be complete.

Experiments on the comparison of the electrical and the osmotic values of the coefficient of ionisation are now seen to have little use from the point of view of the controversialist seeking arguments for or against the ionic dissociation theory. Such comparisons, however, are of interest, inasmuch as they give data which may enable a more complete theory than we yet possess to take account of the inter-ionic forces which seem to disturb the course of the phenomena except at extreme dilution. Taking as an example solutions of potassium chloride, we may compare the ionisations deduced from electrical measurements by the writer at 0° C. with that indicated by the combined cryoscopic experiments of Griffiths, Raoult, Loomis, and H. C. Jones. The coincidence with theory of Griffith's result shows that the two values agree at extreme dilution, but the cryoscopic curve falls below the electrical one at concentrations of about one-hundredth normal and upwards, reaching a maximum discrepancy (0·84 compared with 0·88) at one-fifth normal, and approaching the higher curve again at greater concentrations. It is possible that the two curves, if prolonged, would cross each other at some considerable concentration. Such chance coincidences probably explain some of the agreements which have been observed between the two lines of research in moderately strong solutions of many salts. More accurate determinations of freezing-points are needed before such comparisons as these can be taken as a satisfactory basis for theoretical generalisations. Collections of present data have been made by MacGregor (*Phil. Mag.*, 1900, [5], l., 505), and by Kahlenburg (*Journ. Phys. Chem.*, 1901, v., 399), and further discussion can be found in the writer's book on the "Theory of Solution" (Cambridge, 1902).

The modern theory of the galvanic cell, based on that of the concentration cell, involves both electric and thermodynamic considerations. By imagining an isothermal and reversible cycle, carried out by the passage of one electric unit through the cell, and the reversal of all the chemical and concentration changes by other means, the electric work, and thus the electromotive force, can be calculated. The original treatment of the subject, due to von Helmholtz, effected the reversal by an imagined process of evaporation and condensation of vapour, but it is now more usual to suppose that the reversal is brought about by producing the necessary changes of concentration by osmotic means. In one or other of these ways, by assuming the gaseous laws, the work done in the second part of the cycle can be calculated, and this is equal to that given out in the first part. It is evident that such a theory, based on the principles of theormodynamics alone, furnishes no evidence, one way or the other, about any definite electrolytic or ionic hypothesis, any more than the thermodynamic theory of osmotic pressure can enable us to decide whether that pressure is produced by chemical affinity or by the bombardment of the membrane by the dissolved molecules. In each case we may either rest content with the correlation of the subject given by thermodynamics, or we may inquire further whether any known picture of the physical nature of the phenomena will give us a satisfactory explanation.

Now one kind of concentration cell may be regarded in a simple manner from the point of view of the dissociation theory. It is a cell in which the total potential difference is that due to the contact of two solutions of the same substance at different concentrations. Let us imagine a strong solution of hydrochloric acid placed in a vertical cylinder, and a volume of water placed above it. The dissociated ions of the acid will both diffuse upward, but the more mobile hydrogen will travel faster than the chlorine. Separation thus occurs, and the water (or dilute solution) is found to take a positive potential relatively to the strong solution. Soon, however, the electrostatic forces between the ions become so great that further separation is impossible, and the opposite ions then diffuse at equal rates. From Kohlrausch's experiments we know the velocity with which any ion moves under the action of a given force, and from a knowledge of the osmotic pressure gradient we can calculate the forces at work. Thus the actual velocities of diffusion can be obtained, and the diffusion constant deduced. It is found to agree in a remarkable manner with the observed diffusivity. Equating the velocities of the two ions we get the condition for no further separation, and obtain an expression for the difference of potential between the two solutions in the form—

$$\frac{R\,T}{q}\,\frac{v-u}{v+u}\log\frac{c_2}{c_1},$$

where R is the gas constant for 1 grm.-molecule and of its electric charge, T the absolute temperature, c_1 and c_2 the concentrations, and u and v the coefficients of ionic mobility. Such an expression agrees with that deduced thermodynamically for similar cells, and Nernst, by suitable experimental arrangements, has confirmed it directly. Thus the phenomena of concentration cells may be satisfactorily explained by the hypothesis of independent ionic diffusion.

The chemical reactions of electrolytes, rapid and easily produced, are in marked contrast with those of organic bodies, which are usually attacked slowly and with difficulty. In the original presentment of the dissociation theory Arrhenius pointed out the close numerical con-

nection which exists between the electrical ionisation of aqueous solutions and the coefficients of chemical activity of the dissolved substances.

There is no such definite theoretical deduction of this relation as of that between the conductivity and osmotic effects; the connection of electrical ionisation with chemical activity is a matter of observation, and the conclusion that in the rapid chemical actions characteristic of electrolytes it is the ions which alone are active, rests on the evidence of this connection alone. The numerical relations given by Arrhenius, and the many deductions from this hypothesis which have been verified for aqueous solutions, have led to the idea that a similar explanation of the nature of all rapid chemical action might be given, whatever the solvent and whatever the conditions. There seems, however, no valid theoretical reason which necessitates such an extension, and it is possible that in other solvents, and for gaseous or fused systems, rapid chemical change may be brought about by non-electrical double decomposition. This conclusion is supported by an observation of Kahlenberg on the instantaneous production of a precipitate of copper chloride when hydrochloric acid is passed into a non-conducting solution of copper oleate in benzene (*Journ. Phys. Chem.*, 1902, vi., 1). It is evident that such a result indicates that in the particular solvent used rapid chemical action may occur which is not correlated with appreciable electrolytic ionisation, but it does not in the least affect the electrical and osmotic evidence we have adduced above in favour of the theory of the ionic dissociation of the aqueous solutions of electrolytes. Nevertheless, it serves to caution us against extending the deductions of theory which apply to simple aqueous solutions to cases which have not been subjected to an adequate theoretical and experimental examination.

The recognition of the intimate connection between chemical and electrical phenomena led Ostwald to apply the mass law of chemical action to the effect of dilution on the equilibrium between the undissociated molecules and the ions formed from them in an electrolytic solution. As is well known, this application met with perfect success in the case of weak acids and other slightly conducting solutions, but completely failed to explain the effects of dilution on strong acids and other good conductors. This discrepancy has been considered one of the greatest objections to the dissociation theory. The difficulty, which formerly appeared to the writer a very great one, is probably to be explained by that difference in the law of the variation of the force with the distance which we have already pointed out must exist between solutions containing non-dissociated bipolar molecules and those containing dissociated electrified ions. The inter-molecular forces, varying inversely as the fourth power of the distance, rapidly become insensible with dilution, while those between the ions, depending on the square of the distance, are effective at much higher concentrations. Now the theory of the mass law rests on a thermodynamic basis, and in its deduction the assumption is made that the matter considered is in the dilute state. The work done in forming a small quantity of one of the products of the reaction at a standard pressure, and bringing it to the existing pressure, may then be written in the form $a + RT \log b\ c$, where a and b are constants, R the gas constant for 1 grm.-molecule, T the absolute temperature, and C the concentration. Similar expressions give the work done for other reagents or products, reckoned positive when they are formed, and negative when they disappear. When equilibrium is reached, the change of available energy arising from a further slight transformation must vanish, thus the value of $n_1(a_1 + RT \log b_1c_1) + n_2(a_2 + RT \log b_2c_2) + \ldots$ must be zero, and we see that $C_1^{n_1} C_2^{n_2} \ldots$ may be put equal to K, a function of the temperature alone. This result is the mass law, and if we apply it to a solution in which 1 grm.-molecule of electrolyte is dissolved in a volume V, a faction α being ionised, we obtain the equation

$$\left(\frac{1-\alpha}{V}\right)^{-1}\left(\frac{\alpha}{V}\right)^{2} = \frac{\alpha^2}{V(1-\alpha)} = K,$$

Ostwald's dilution law. Its deduction clearly involves the assumption that the gas laws hold good, and that consequently no inter-molecular forces or other similar actions are appreciable. We must not, therefore, look for conformity with the dilution law in solutions where many dissociated ions are present.

Summing up our inquiry as far as we have yet pursued it, we may say that the phenomena of electrolysis, and the osmotic properties of electrolytes, clearly indicate that the conduction of a current through an aqueous solution consists in the convection of charged ions through the liquid, the ions being dissociated from each other while they are electrolytically active.

We must now raise the much wider question, and ask whether this mode of conduction is a universal accompaniment of electrolysis, or whether it is confined to the case of solutions in water. Since the development of the dissociation hypothesis, as applied to liquid electrolytes, a vast increase has occurred in our knowledge of the discharge of electricity through gases. This process has been satisfactorily explained as a convective electrolytic action, the ions being in some cases dissociated molecules, in other cases isolated corpuscles, which may represent the ultimate units of negative electricity, perhaps even the common constituents, aggregates of which make up the different chemical atoms. Such results not only support the idea of a similar dissociation as the cause of the conductivity of solutions, but give a presumption in favour of the general applicability of such theories. When, however, we examine how far such a presumption is justified, further considerations are seen to be involved. Had the phenomena of gaseous conduction been first in the field, we could not, without experimental evidence, have extended a dissociation hypothesis, framed to explain them, to the much more complicated systems which are formed by electrolytic solutions. It is only on the knowledge summarised in the laws of Faraday, Ohm, and Kohlrausch, that the particular phenomena which have led us to the dissociation theory require such an explanation, and at present, it is only for solutions in water, and a few other liquids, that we possess sufficient evidence for those laws, and for the other relations to which we have referred, to enable us to draw valid conclusions. Without definite experimental evidence in each case, we cannot legitimately extend these conclusions, and when, as in fused salts, the conditions are entirely different, we shall presently see that an alternative explanation is possible. Nevertheless, for all *solutions* which conduct electricity, the presumption in favour of similarity of explanation is very great, and for several solvents, at any rate, experiments show that the general process of conduction is similar to that which we have studied in aqueous solutions.

When we go further, however, and try to trace in non-aqueous media the ionisation of solutes as measured electrically and osmotically, we are met by want of numerical data, largely owing to increased difficulty of experiment. With some solvents, as, for instance, the alcohols, freezing-point work is impossible, and in no case do measurements of osmotic properties appear to have been made at dilutions great enough to enable us to fairly treat the systems as thermodynamically dilute. On the electrical side more data are available, but the examples of acetic acid and ammonia show that, even in water solutions, complete ionisation cannot always be experimentally attained, and, without definite evidence, it is not safe to conclude that in another solvent it can ever be reached. We have already seen that only when the dissociation is complete can a just comparison be made between the numbers of ions given by a molecule as determined electrically and as determined osmotically. Thus it is necessary to push the dilution so far, that the equivalent conductivity reaches a definite limiting value before making such comparisons. Limiting values have been obtained for salts of the alkali metals dissolved in methyl and ethyl alcohols (Fitzpatrick, *Phil. Mag.*, 1887, xxiv., 378; Völlmer, *Wied. Ann.*, 1894, 328; Zelinsky and

Krapiwin, *Zeit. Phys. Chem.*, 1896, xxi., 35), in acetone (Carrara, *Gazz. Chim. Ital.*, 1897, xxvii., i., 207; Laszozynski, *Zeit. Elektrochem.*, 1895, II., 55; Dutoit and Aston, *Comptes Rendus*, 1897, cxxv., 240), and in pyridine (Laszozynski and Gorski, *Zeit. Elektrochem.*, 1897, IV., 290), but in all these cases no osmotic data have been determined at dilutions great enough to secure complete ionisation, or to justify the gaseous laws as applied to the osmotic phenomena. Experiments at higher concentrations are of little value, for not only do the disturbing causes already noted in the case of aqueous solutions act here also, but it is known that one of them, the influence of complex ions, is much more common and much more important. (Comparisons of electric and osmotic data for non-aqueous solutions have been collected by Lincoln, *Journ. Phys. Chem.*, 1899, iii., 457). It is probable too that association of the non-ionised solute molecules may occur, Kahlenberg, for instance, having discovered cases in which the boiling- or freezing-points of conducting solutions indicate that the number of such molecules is less than the chemical formula would lead one to expect (*Journ. Phys. Chem.*, 1901, v., 342). It is evident that the existence of such association does not in the least prevent the conduction of the current by the movement of charged ions dissociated from each other. Such observations as those referred to have been brought forward as evidence against the whole basis of the theory of ionic dissociation, but the relations on which they bear are, as we have seen, merely consequences of the theory under ideal conditions of very restricted nature, and are not, as seems to be so commonly supposed, the very foundation on which the theory rests.

Faraday found that many fused salts were electrolytes, with conductivities of the same order as those of aqueous solutions, and since his time it has been confirmed that, in such cases, the electro-chemical equivalents have the usual values (Faraday, "Experimental Researches"; Helfenstein, *Zeit. Anorg. Chem.*, 1900, xxiii., 255). How far are the principles of the dissociation theory applicable to fused electrolytes? No osmotic data are available, and it is difficult to see how such data could be obtained. Let us examine the matter from the electrical side. The products of decomposition appear at the electrodes only, and Faraday's laws hold good; hence the process must be convective, but we have no knowledge of the ionic velocities, and no means of estimating the amount of ionisation. When closely scrutinised, the conditions are seen to be essentially different from those which led to the adoption of the belief in considerable and permanent dissociation for aqueous solutions. We do not know that the conductivity is proportional to the number of ions present, but even if such a relation were established, the consequences deduced from it in the case of solutions would not necessarily follow. The process, as we said, must be convective, and freedom of migration of the ions is necessary, but, unlike a solution, a fused salt consists of a collection of molecules all of the same kind, and the argument from the frequency of collision between dissolved molecules, isolated from each other by comparatively vast spaces of solvent, ceases to be valid. In a fused salt the electrolytic molecules are crowded together, and, even if dissociated ions are present, the interaction of one of them with one of the surrounding electrolytic molecules, which replace the neutral molecules of the solvent of a solution, would make possible an effective interchange, and enable an electric transfer to take place. Thus the frequency of interchange for any one ion would not increase with the ionic concentration as in the case of a solution, and the conductivity might be proportional to the number of ions without permanent ionic dissociation. The conditions are entirely different to those which hold in a solution, where the solvent molecules are of different kind to those of the electrolyte and cannot take a direct part in the electrolytic process. We may now go further, and say that it is possible that conduction in a fused salt may be due to a mere possibility of interchange between the electrified parts of the molecules, without any permanent and definite dissociation. Some process in the nature of Grotthus's chain may, in this case, secure the migratory freedom necessary for electrolytic conduction. Whether this is so, or whether, as in solutions, the current is carried by ions dissociated from each other, their number being a function of the temperature, remains a question for future investigation.

THE PHENOMENA OF LUMINOSITY AND THEIR POSSIBLE CORRELATION WITH RADIO-ACTIVITY.*

(Dynamic Isomerism in relation to Luminous Phenomena).

By HENRY E. ARMSTRONG, F.R.S.,
and
T. MARTIN LOWRY, D.Sc.

The possibility of regarding *luminous manifestations* generally—including radio-activity—as the outcome of oscillatory changes in molecular structure, has already been pointed out by one of us in a communication made to the Society more than a year ago, in which the kind of change contemplated was exemplified by reference to the case of nitrocamphor (Henry E. Armstrong, "The Conditions Determinative of Chemical Change and of Electrical Conduction in Gases and on the Phenomena of Luminosity," *Roy. Soc. Proc.*, 1902, vol. lxx., p. 99; Chemical News, vol. lxxxv., p. 241). As the phenomena of radio-activity are exciting so much interest, it appears desirable to enter somewhat more fully into an explanation of the argument underlying this conception of the origin of luminous appearances.

In the note referred to, it was suggested that *tribo-luminescent* substances, *i.e.*, substances which become luminous at the moment of crushing, might conceivably, at the same time, manifest radio-activity. Sir William Crookes has recently examined saccharin from this point of view, using freshly prepared crystals which one of us had placed at his disposal. We are much indebted to him for the following account of his observations:—

"The crystals of saccharin, when broken in the dark, gave off flashes of light.

1. A sensitive photographic film was covered with a sheet of aluminium foil 0·04 m.m. thick, and some crystals were broken on the foil. On development no darkening was seen.

2. A similar experiment, in which black paper was used instead of aluminium foil, also gave negative results.

3. Some crystals of saccharin were broken close to the sensitive surface of a photographic film. The flashes of light could be seen through the film. On development some spots were seen on the film, which were caused probably by the light given off,

4. A crystal was broken near the surface of a barium platinocyanide screen. The screen glowed at the moment of the flash from the crystal.

5. A crystal of saccharin was put on a hard surface and a screen of barium platinocyanide was laid face upwards on it. By means of pressure on the screen the crystal beneath was crushed, when a flash of luminosity was seen to cover the screen over the place where the crystal was broken.

6. A screen of hexagonal blende was taken, and Experiments 4 and 5 were repeated with it. The results were negative, except that I fancied there might be a trace of light when the crystal was broken close to the sensitive surface of the screen."

Although it may be argued from Experiment 5 that saccharin is radio-active when crushed, we have been unable hitherto to detect any effect on the electrometer. Through

* A Paper read before the Royal Society, June 18, 1903.

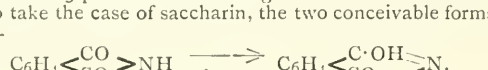
the kindness of Dr. Lapworth we have been able also to examine the menthyl phenylformylacetate recently described by him, a substance capable of existing in isodynamic forms, which is not only intensely tribo-luminescent, but gives out most brilliant flashes of light as it separates from solution, its behaviour in this respect being, if possible, even more striking than that of radium in face of a screen of hexagonal blende to which Sir William Crookes has directed attention. As a small quantity of this substance was crystallising out from petroleum spirit, no fewer than ninety-two flashes were observed in broad daylight in the course of ten minutes. Even this substance, however, has not hitherto given positive results when tested by the electrometer.

Tribo-luminescence.

We have now to consider the nature of the change involved in the production of the luminous flash, in order that it may be clear why, in our opinion, if radio-activity were observed in such a case, it would have been as the concomitant to chemical change.

There is distinct evidence that the phenomena of tribo-luminescence may be correlated with the occurrence of the form of isomeric change which attends the passage of a compound into the isodynamic* form of low potential. Tschugaeff (*Ber.*, 1901, vol. xxxiv., p. 1820), who has examined over 500 inorganic and organic compounds, found that about 25 per cent of the latter gave a more or less intense flash when crushed; of these a considerable proportion appear to be such as could exist in isodynamic forms. Only about 5 per cent of the inorganic substances flashed.

To take the case of saccharin, the two conceivable forms are—

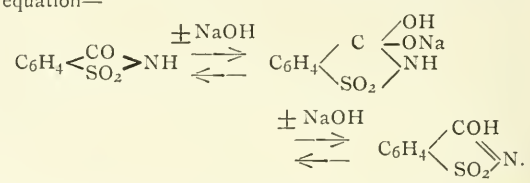


Comparable with these are the two isodynamic forms of π- and β-bromonitrocamphor, for example—

Normal neutral form. Pseudo acid form.

In the solid state both forms of π-bromonitrocamphor are stable: when either form is dissolved in a liquid, isomeric change sets in; sooner or later, it may be only in the course of a few hours or even days, a state of equilibrium is established, about 6 per cent of the material being present in the pseudo-form and 94 per cent in the normal form (compare Lowry, *Trans. Chem. Soc.*, 1898, p. 966; *Proc. Chem. Soc.*, 1903, p. 129). The change, however, does not occur spontaneously, but is undoubtedly dependent on the presence of a catalyst, as equilibrium is established with great rapidity if a trace of alkali be added; acids have only a slight, although definite, accelerating effect. In the case of β-bromonitrocamphor, solutions in benzene of the neutral as well as of the acid form which have been kept during several days without undergoing change, when transferred to another vessel, have rapidly passed to a condition of equilibrium—doubtless because this vessel had been less successfully cleansed than that first used. It can, therefore, scarcely be doubted that the change occurs within a complex system—one which, it is only reasonable to suppose, constitutes an electrolytic circuit. The process is reversed when crystallisation sets in; if the evaporation of the solvent take place sufficiently slowly, the whole of the material is converted into and crystallises out in the less soluble form; if, however, evaporation take place rapidly, the isomeric change may lag behind the crystallisation and both forms may separate. In the case of nitrocamphor, the normal form is the one that separates from the solution; but in the case of π- and β-bromonitrocamphor, although the pseudo-form is the minor constituent in the solution, being much less soluble than the isomeride, it is one to separate on crystallisation.

The passage of the one form into the other in the case of saccharin, for example, may be pictured as involving the occurrence of changes such as are represented in the equation—

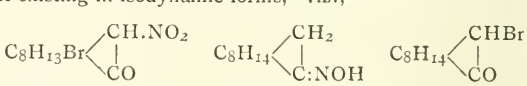


Supposing the stable form of lower potential to crystallise out, the crystals, in almost every case would contain a minute and variable amount of the isodynamic form entangled, as it were, in the mass. In the solid, reversion to the stable form would take place very slowly. Presumably, however, sudden crushing of the crystals would afford opportunity for the change to take place and for the sudden *liberation of energy*—hence the momentary flash.

In support of this view we have the fact:—

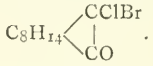
1. That the phenomenon of tribo-luminescence occurs irregularly in the case of saccharin: being sometimes shown by one crop of crystals and not by another, the highly purified substance—Professor Pope informs us—being inactive.

2. That whereas the phenomenon is observed in the cases of three derivatives of camphor which are obviously capable of existing in isodynamic forms,* viz.,—



π-Bromonitrocamphor. Camphoroxime. α-Bromocamphor.

it is not seen in the case of camphor derivatives, which, although otherwise similar, cannot exist in isodynamic forms, *e.g.*, α-chloro-α-bromocamphor,—



It is not, at present, necessary to assume that the phenomena are limited to cases of isomeric change; obviously, changes such as those above considered, may be regarded broadly as dissociative or reversible changes; and from this point of view, it is sufficient to regard the phenomena as the outcome of a loss of potential consequent on the passage from an unstable to a stable system. Thus, if Tschugaeff's statement that a salt such as aniline hydrochloride is tribo-luminescent, be confirmed by observation with the highly purified substance, it will be justifiable to assume that when it is crushed, the manifestation of luminosity may be due to the reformation of salt momentarily dissociated by pressure.

From the point of view here advocated, it would be impossible to construct a condenser from a *pure* dielectric; and if the dielectric of a charged condenser were suddenly smashed under suitable conditions, it might exhibit the phenomenon of triboluminosity and perhaps radio-activity.

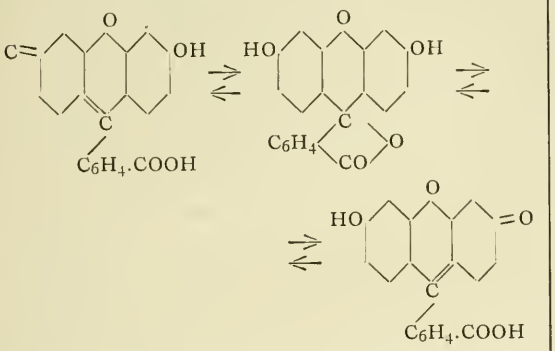
Fluorescence.

It was originally suggested by one of us, in discussing the origin of visible colour, that fluorescence is the "beginning of colour." Subsequently, Dr. J. T. Hewitt, in a paper on the relation between constitution and fluorescence, published early in 1900 (*Proc. Chem. Soc.*, 1900 vol. xvi., p. 3; *Zeit. Phys. Chem.*, 1900, vol. xxxiv., p. 1), took the important step of associating the appearance of

* This term has been introduced by one of us as being more appropriate than the term tautomeric to connote substances which are apparently almost equipotential—as they so closely simulate one another in behaviour under ordinary circumstances—and are easily interconvertible.

* Nitrocamphor does not flash when crushed; perhaps this is because of its texture. It may be that the effect will be observed at lower temperatures.

fluorescence, not with the mere occurrence of the quininoid type of structure, which one of us has long contended is characteristic of visibly coloured substance, but with the continued *development* of such a structure—in other words, he has regarded it as the outcome of oscillatory changes in the course of which a non-quinonoid compound undergoes conversion into the isodynamic quinonoid compound,* for example, in the manner represented by the formulæ, which picture the changes undergone by fluorescein :—



According to Hewitt, "all the molecules will be undergoing tautomeric change continuously and frequently, and energy absorbed when the molecules have one configuration will be, to an appreciable extent, emitted when they correspond to the other configuration. It is practically certain that the vibration frequency of fluorescein is different in the two states, and hence every opportunity is offered for energy of a rapid vibration frequency to be largely transformed into energy of greater wave-length."

Hewitt obviously does not regard fluorescence as a "flash phenomenon," but as a form of colour, as it were.

While agreeing with Hewitt that the origin of the effect is to be sought in the occurrence of reversible changes involving the production of dynamic isomerides, we think that fluorescence is to be regarded as something apart from colour, which, more often than not, is superposed upon colour. Colour appears to be dependent upon selective absorption, and scarcely to involve any *return* of the absorbed energy as light. The character of the colour effect in fluorescence is quite distinctive; it is not only remarkable on account of its intensity, but there is in it an indefinable qualitative difference which seems to separate it from ordinary colour. If regarded as a "flash phenomenon" this difficulty disappears.

Hewitt appears to regard fluorescence as the outcome of mere intramolecular wobble. To us it seems likely that the change is conditioned by a catalyst, and that it occurs within a complex electrolytic circuit. From this point of view, the fluorescence of uranium glass is noteworthy, as showing that changes in molecular structure may go on in a solid viscous medium. It will be desirable to ascertain whether such glass is fluorescent at low temperatures, at which it ceases to be viscous.

Phosphorescence.

The phenomena of phosphorescence need to be considered with reference both to cases in which the manifestation attends oxidative or other kinds of chemical change (the glow of phosphorus, the glow-worm, phosphorescent bacteria), and to those in which it is induced by exposure to light (luminous sulphides). The former might well almost be regarded as cases of fluorescence, as a continual supply of energy is derived from the continued occurrence of a chemical change involving loss of energy. With regard to the latter, it would seem that it is not a property of pure substances. Thus it is known that the production of sulphides, which can be rendered luminous by exposure to light, is dependent on certain special conditions being fulfilled, that, for example, barium sulphide, which is not sensitive *per se*, becomes highly so when it is associated with a minute proportion of bismuth.*

The phosphorescent medium may be pictured as a complex system, capable of undergoing "electrolytic" deformation under the influence of light of high refrangibility: as the changes thus induced are reversed, the energy stored up during insolation becomes liberated, and the persistence of the effect is but a consequence of the fact that the change takes place under restraint, in a viscous medium.

Dewar's remarkable observations on phosphorescence at low temperatures clearly foreshadow the conclusion that the property is to be correlated with structure. The two most remarkable classes of substances, he states, are the Platinocyanides amongst inorganic compounds, and the Ketonic compounds amongst organic. But these latter are precisely those which are most prone to undergo conversion into isodynamic forms. It is very noteworthy that, according to Dewar, "water when pure is only feebly phosphorescent, but remarkably so when impure."

Radio-activity.

Pursuing the argument a stage further, it appears to us justifiable to regard the activity of radium tentatively, as but an exaggerated form of fluorescence, in which radiations unnoticed by substances generally—capable of penetrating substances generally — become absorbed and rendered obvious. Such an explanation, from the chemist's point of view, is at least as rational as one which assumes that nature has endowed radium alone of all the elements with incurable suicidal monomania, especially as exothermic changes, when once started, have a tendency to occur rapidly, if not explosively.

There seems to be no good reason for assuming that in fluorescent and other ordinary substances, we possess screens capable of arresting rays of every conceivable kind; it may well be that our knowledge of solar radiations is not yet complete; that radium should be more powerful than other substances is not surprising, seeing that of all the elements known to us, it perhaps has the highest atomic weight. It is also worth noting that radium stands in close relation to the elements which afford luminous sulphides.

With regard to "Thorium and Thorium X," the facts, as stated by Rutherford and Soddy, do not seem to be incompatible with the view that these are but isodynamic forms of thorium or their equivalent, their behaviour being very similar to that of the isodynamic forms of nitrocamphor, the rate of decay and recovery of activity proceeding according to a simple logarithmic law, just as does the conversion of one form into the other in the case of nitrocamphor. In any case, it appears desirable to approach the problem from this point of view, and to investigate the phenomena far more thoroughly on the chemical side.

Finally, it may be pointed out that the properties discussed in this note are common to not a few substances. Uranium nitrate is not only radio-active, but tribo-luminescent, fluorescent, and phosphorescent, at low temperatures; and, as Dewar has shown in a recent Royal Institution lecture, it becomes highly electrified when cooled. Platinocyanides also are tribo-luminiscent, fluorescent, and phosphorescent, at low temperatures.

* In this connection, attention may be called to the following passage which occurs in a note by one of us on fluorescence in quinine salts (*Trans. Chem. Soc*, 1892, p. 790):—"It is well known that the oxy-salts of quinine are alone fluorescent, salts like the chlorhydride not being so; it is conceivable that this is due to the inferior stability of the former in solution, and that, owing to the occurrence of dissociation, a condition is engendered favouring the passage by dynamic change from the non-fluorescent centric to the fluorescent ethenoid condition.

* L. E. O. de Vlsser, *Rec. Trav. Chim.*, 1901, vol. xx., p. 435; 1903, vol. xxii., p. 133. In the case of calcium sulphide, the maximum effect is produced when about 1 atom of bismuth is present to 50,000 of calcium. According to the later paper, bismuth alone does not confer the property, but the presence of a sodium salt in addition makes the mixture sensitive.

That the several manifestations all have their origin in the formation and decay of isodynamic or equivalent systems, is therefore by no means improbable.

Whatever the ultimate value of the considerations advanced in this note, they at least serve to show that much may be learnt by further study of the extent to which luminous phenomena generally are to be correlated with structure and structural changes.

REPORT ON THE SEPARATION OF NITROGENOUS BODIES.*

By L. L. VAN SLYKE.

(Concluded from p. 81).

9. *Determination of Nitrogen in the Form of Peptones.*

(1) *By Tannin and Sodium Chloride.*

We place 100 c.c. of our water extract of cheese in a 250 c.c. graduated flask, add 1 grm. of sodium chloride and a solution containing 12 per cent of tannin until one drop added to the clear supernatant liquid gives no further precipitate. We then dilute to the 250 c.c. mark, shake, filter through a dry filter, and determine the amount of nitrogen in 50 c.c. of the filtrate by the Kjeldahl method; this gives us the amount of nitrogen in the form of amido-acid and ammonia compounds. The amount of nitrogen in the form of peptones is determined by difference—that is, by subtracting from the amount of total nitrogen in the water extract the combined sum of the amounts of nitrogen found in 5, 6, 7, 8, and 10.

The combination of tannin and salt has been settled upon by us as the most satisfactory for the separation of casein-derived peptones from amido-acid compounds in milk and cheese analysis, when, as is commonly the case, we have large amounts of amido-acid compounds relative to peptones. We have confirmed Schjerning's (*Zeit. Analyt. Chem.*, 1900, xxxix., 545) results showing that this reagent does not precipitate the monoamido-acid compounds, such as leucin, tyrosin, aspartic acid, glutamic acid, and amido-valeric acid, nor does it precipitate histidin, arginin, lysin, cadaverine, putrescin, lysatin, or ammonia. In our work the tannin-salt solution has nearly as great a precipitating power as phosphotungstic acid, precipitating 93·3 per cent of the total nitrogen compounds present in a sample of fresh milk; in a study of ripened cheese it precipitated the uncrystallisable end products, caseoses and peptones, so completely that no further trouble was experienced in separating the crystallisable end products.

It is well to record here the fact that when precipitation of peptones with tannin-salt solution is attempted in a mineral acid solution no precipitate occurs; it is only in neutral solution that more complete precipitation takes place.

The chief objection to the use of tannin-salt solution as a means of separating caseoses and peptones from amido-acid compounds and ammonia is that it is not a complete precipitant of peptones. Hence, when the reagent for this separation is used we commonly leave some peptones to be estimated as amido-acid compounds, the amount of peptones thus being made smaller, and the amount of amido-acid compounds larger than the quantity actually present. Under the discussion of the use of phosphotungstic acid as a reagent for separating these classes of nitrogen compounds are given for comparison some results secured by each of the two reagents.

(2) *By Phosphotungstic Acid with Sulphuric Acid.*

In a 250 c.c. graduated flask we place 100 c.c. of the water extract of cheese, add 100 c.c. of water, and then 5 c.c. of strong sulphuric acid. To this add phosphotungstic acid of 30 per cent strength until one drop gives no further precipitation in the clear supernatant liquid. Then dilute to the 250 c.c. mark and filter through a dry filter. In 50 c.c. or 100 c.c. of this filtrate we determine the amount of nitrogen by the Kjeldahl method, and then the amount of peptones is obtained by difference.

Phosphotungstic acid has come into very general use in this country and in Europe as a means of separating peptones from amido-acid compounds in work with cheese and milk. The results of Stutzer (*Zeit. f. Analyt. Chem.*, 1896, xxxv., 1493) and of Bondzynski (*Landw. Jahrbuch der Schweiz*, 1894) agree in showing that phosphotungstic acid is a complete precipitant of casein, caseoses, and peptones, while in their experience it does not precipitate the amido-acid compounds or ammonia. Freudenreich and Jensen in all their work, even of recent date, have used this reagent in the cold as a means of separating peptones from amido-acid compounds. Babcock, Russell, and Vivian, in this country have used it, as well as tannin, designating the different precipitates as "peptones by phosphotungstic acid" and "peptones by tannin."

In the introductory portion of this paper, when mentioning different cleavage products of casein, we included among them the hexon bases, viz., arginin, histidin, and lysin; and, in addition, certain compounds resulting from their cleavage, such as putrescin and cadaverin, and also pyrrolidin-*a*-carbonic acid, all of which are precipitated by phosphotungstic acid. While all these products have not been separated from ripening cheese, it is probable that they will be sooner or later. We shall soon publish results of work done in this laboratory showing in normal ripening cheese the presence of histidin, lysin, putrescin (derived from arginin) (A. Ellinger, *Ber.*, 1898, xxxi., III., 3183), and Siegfried's lysatin, which is also precipitable by phosphotungstic acid. The quantities of these bases that can be derived from casein are not to be neglected, since, for example, in a hydrochloric acid cleavage 15·4 per cent of the nitrogen of the products splits off into the hexon bases. Bondzynski has used phosphotungstic acid in hot solution with arginin, and finds the precipitate soluble when hot, separating out on cooling; and this statement we can confirm, the solution, however, being complete only on boiling. In the case of lysin, histidin, and putrescin the phosphotungstic acid precipitate fails to redissolve completely at the temperature of the water-bath or on boiling. This behaviour renders worthless the use of phosphotungstic acid as a reagent for the separation of peptones from those amido-acid compounds that are precipitated by it.

We have seen that tannin-salt solution fails to precipitate peptones completely, and that phosphotungstic acid precipitates, in addition to peptones, some amido acid compounds. When, therefore, we use these two reagents in precipitating solutions that contain both peptones and amido-acid compounds, as in the case of normal ripening cheese, we should expect to find the amount of nitrogen compounds left in the filtrate less with phosphotungstic acid than with tannin. This is found invariably to be the case. Vivian ("Ann. Rep. Wis. Exp. Sta.," 1899, xvi., 171) has published some results obtained with nine different cheeses, which illustrate this point. We give his figures in the table following:—

TABLE I.—*Comparison of Phosphotungstic Acid and Tannin-salt Solution in Precipitating the Nitrogen Compounds contained in Water Extracts of Cheese.*

Sample No.	Precipitating agent used.	
	Phosphotungstic acid.	Tannin-salt solution.
	Per cent.	Per cent.
1.	1·08	1·54
2.	1·00	1·26
3.	0·82	1·12
4.	0·63	0·65
5.	0·67	1·16
6.	1·69	1·87
7.	0·95	1·08
8.	1·10	1·36
9.	1·22	1·42
Average ..	1·02	1·27

* Proceedings of the Nineteenth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, D.C.

In connection with the above results nothing was stated in regard to the history of the cheeses used in the work. We have studied the action of phosphotungstic acid and tannin-salt solution in connection with samples of cheese that were under known well-controlled conditions, thus learning something of the general character of the proteolytic changes taking place. Twenty-five grms. of cheese curd were placed in each of several Erlenmeyer flasks, 50 c.c. of water added, and the contents sterilised by heat. We then added 0·5 grm. of concentrated lactic acid, in order to convert the paracasein into unsaturated paracasein lactate ("N.Y. Agr. Expt. Sta.," 1902, ccxiv., 67). To some of the flasks thus prepared sterilised pepsin was added, and to others sterilised rennet extract. For this purpose the enzymes were prepared as follows:—We dissolved 600 m.grms. of Parke Davis and Co.'s aseptic pepsin in 25 c.c. of water, added 0·5 per cent of formalin containing 40 per cent of formaldehyde), and let the solution stand until bacteriological examinations, made by Mr. H. A. Harding, showed the absence of living organisms. The mixture was then diluted to 100 c.c. with water, and to each flask containing cheese we added 10 c.c. of this sterilised pepsin solution. One thousand parts of the mixture in each flask thus contained one part of pepsin.

In preparing the sterilised rennet solution, 5 c.c. of Hansen's rennet extract were diluted to 25 c.c. with water, 0·5 per cent of formalin was added, the completeness of sterilisation proved by bacteriological examinations, diluted to 100 c.c., and 10 c.c. of this preparation added to each flask containing cheese.

The flasks thus prepared were kept at 15·5° C. The analytical results given below were obtained at the end of two and four weeks. In this work, we had only the enzymes of pepsin and of rennet pepsin acting upon our proteid. Under these conditions, especially in the given length of time, we should not expect the formation of any considerable amount of amido-acid compounds precipitable by phosphotungstic acid. The results obtained are given in the following table:—

Table II.—*Comparison of Phosphotungstic Acid and Tannin-salt Solution in Precipitating the Nitrogen Compounds Formed by Peptic Digestion of Cheese.*

Sample No.	Precipitating agent used.	
	Phosphotungstic acid.	Tannin-salt solution.
	Per cent.	Per cent.
1.	0·10	0·45
2.	0·10	0·44
3.	0·150	0·645
4.	0·175	0·685
5.	0·10	0·48
6.	0·08	0·46
7.	0·16	0·73
8.	0·16	0·70
Average ..	0·123	0·574

In every case except one, the amount of nitrogen not precipitated by tannin-salt solution was more than four times the amount obtained by phosphotungstic acid. No ammonia was present in any case. In view of these widely differing results in relation to the amounts of amido-acid compounds found, the questions may be asked:—"Which reagent more nearly represents the amount of amido compounds actually present? Does the tannin-salt reagent fail to precipitate the peptones completely, thus allowing the unprecipitated peptones to be counted among the amido acid compounds? Or does the amount of nitrogen in the filtrate in case of this reagent really represent amido-acid compounds? Does the phosphotungstic acid precipitate some of the amido compounds simultaneously with the peptones, thus cutting out a part of the amido-acid compounds and counting that part among the peptones? Or is there in the cheese only the small amount of end products indicated by the action of the phosphotungstic acid?"

While we did not by individual isolation determine to what extent amido compounds were present, we are justified in believing that such compounds were not yet present in the cheese in any appreciable degree; and, hence, the figures obtained with phosphotungstic acid are much nearer the truth than those obtained by tannin-salt precipitation. The reasons for this belief are as follows:—The amido compounds precipitated by phosphotungstic acid are known to be chiefly the diamido compounds, while the monoamido compounds are precipitated little, if at all. Hence, the compounds found in the filtrate of a phosphotungstic acid precipitation are mainly monoamido compounds. Now let us assume temporarily that the amounts of nitrogen in the tannin-salt filtrate, given in the table above, represent the total amido compounds, free from peptones; then, since the monoamido compounds are represented by the amounts of nitrogen obtained in the phosphotungstic acid filtrate, the difference between the two sets of figures—that is, those obtained by tannin-salt solution and those obtained by phosphotungstic acid—represents the amount of diamido compounds. Taking the average of the results given in the table above, the nitrogen of the total amido compounds is 0·574 per cent of the cheese, while the nitrogen of the monoamido compounds is 0·128 per cent of the cheese, thus leaving the difference as the nitrogen of the diamido compounds, equivalent to 0·446 per cent of the cheese. According to these figures, the monoamido compounds constitute about 22 per cent of the entire amount of amido bodies, while the remainder, 78 per cent, represents largely diamido compounds. In this case, the ratio of monoamido to diamido compounds is as 1 to 3·5. Keeping these data in mind, we will call attention to some work done by Hart (*Zeit. f. Physiol. Chem.*, 1901, xxxiii., 347) in studying the cleavage end products formed by the action of hydrochloric acid on casein. He found that the diamido compounds formed less than 20 per cent of the total amido compounds, so that the ratio of monoamido to diamido compounds was as 1 to 0·25 or less; in other words, the monoamido compounds were greatly in excess of the diamido compounds, or just the reverse of what we find to be the case in the results embodied in the table above, based on the assumption that the nitrogen in the tannin-salt filtrate represents the total amido compounds and nothing more. The most obvious and rational explanation of this discrepancy observed in the ratio of monoamido to diamido compounds is that it is wrong to assume that the tannin-salt filtrate contains only amido compounds and not any peptones. Withdrawing that assumption, then, and allowing that the nitrogen in the tannin-salt filtrate represents some peptones as well as the amido compounds, how can we tell in this particular case the true amount of amido compounds in the cheese? Unquestionably the results with phosphotungstic acid more nearly represent the truth in regard to the amido compounds, because under the conditions of the experiment we should expect very small amounts of amido compounds, if any; and in this particular case the amounts are so small as practically to indicate the absence of amido bodies altogether. From this it may be seen that it is possible for the tannin-salt reagent to give results that are decidedly misleading.

(3) *By Bromine with Hydrochloric Acid.*

To the filtrate from the zinc sulphate precipitate (7) we add 2 or 3 drops of strong hydrochloric acid, and then bromine until the liquid becomes saturated, and there remains after vigorous agitation an undissolved globule of bromine, amounting to 0·5 c.c. to 1 c.c. This is allowed to stand overnight. The precipitate is then filtered and washed with bromine-saturated water. The nitrogen in the precipitate is then determined by the Kjeldahl method, and is called nitrogen in the form of peptones, the filtrate containing the amido-acid compounds and ammonia.

The use of chlorine by Rideal and Stewart (*Analyst*, 1897, xxii., 228) in precipitating proteids suggested to Allen and Searle (*Analyst*, 1897, xxii., 259) the use of

bromine. They reported that bromine quantitatively precipitates the products formed by the peptic digestion of egg albumin, and they developed the method practically as given above. As applied to the separation of peptones from amido-acid compounds in cheese and milk, the method gives varying results, depending upon the age of the cheese or milk used.

In the case of our water extracts made from cheese nine months to a year old, crystalline bodies in noticeable quantities are precipitated by bromine along with peptones, owing probably to the presence of tyrosin, giving the solution a turbid appearance, and rendering filtration difficult. Schjerning (*Zeit. f. Anal. Chem.*, 1900, xxxix., 545) has shown that tyrosin behaves in this manner with bromine water. This precipitate is partly retained on the filter-paper, and is estimated as peptone.

Schjerning has shown also that bromine does not completely precipitate milk proteids and their derived caseoses and peptones. Of the whole proteid he obtained only 76·7 per cent by bromine. In the case of milk we have obtained results varying with the age of the milk. In perfectly fresh milk, when the amount of amido compounds must have been least, we obtained 91·3 per cent of the entire milk proteids by bromine precipitation. In another case of fresh milk we compared the precipitation of proteids by bromine and hydrochloric acid with that by tannin and sodium chloride, and by solution of phosphotungstic acid and sulphuric acid, with the following results :—There was precipitated—

By phosphotungstic and sulphuric acids, 93·8 per cent of the total nitrogen.

By tannin and sodium chloride, 93·3 per cent of the total nitrogen.

By bromine and hydrochloric acid, 91·5 per cent of the total nitrogen.

There is also a possible source of error in connection with the use of bromine in precipitating peptones when the filtrate from the bromine precipitate is used directly for the determination of amido-acid compounds. We have found in the case of water extracts from cheese over one year old that there is an actual loss of nitrogen when bromine is allowed to stand in contact with the water extract. In the case of one cheese two years old, the cheese extract, consisting of caseoses, peptones, and amido-acid compounds, contained nitrogen equivalent to 2·74 per cent of the cheese before adding bromine, while, after standing one hour in contact with bromine in hydrochloric acid solution, there remained only 1·52 per cent of nitrogen ; in other words, there had disappeared 44·6 per cent of the nitrogen present before the addition of bromine. In cheese one year old we have found the loss varying from nothing in one case to over 5 per cent in others. To show whether or not this loss came from the action of bromine on the caseoses or peptones we removed the caseoses with zinc sulphate, and in another sample of cheese extract we removed the caseoses and peptones with phosphotungstic acid, and the loss still occurred. By passing a current of air through the above extract in contact with bromine and then through potassium hydroxide and through sulphuric acid, these reagents were found free from nitrogen compounds, indicating that the lost nitrogen disappeared in the form of free nitrogen, and not in the form of ammonia or nitrogen oxides. We cannot regard the method of determining the amount of peptones in cheese extracts by means of bromine as a reliable method, because (1) bromine precipitates small amounts of tyrosin, and perhaps certain other similar compounds ; (2) it is not a complete precipitant of caseoses and peptones ; and (3) its filtrate cannot be used for the determination of amido-acid compounds, especially in old cheeses, owing to the decomposing effect of bromine upon such compounds setting nitrogen free. In addition, bromine is a most disagreeable reagent to handle.

(4) *Comparative Value of Different Reagents Used in Separating Peptones and Amido-acid Compounds.*

We have now considered in some detail each of the three reagents most commonly used in separating peptones from amido-acid compounds, viz. :—(1) Tannin-salt solution, (2) phosphotungstic acid with sulphuric acid, and (3) bromine with hydrochloric acid. Tannin-salt solution fails as a perfect reagent for the separation because it does not completely precipitate peptones, which results in making the quantitative results for amido-acid compounds too high, and may indicate the presence of considerable quantities of amido-compounds even when they are practically absent. Phosphotungstic acid, on the other hand, completely precipitates peptones, but also precipitates some of the amido-acid compounds that are present in cheese and milk, and the consequence is that the amount of amido-acid compounds found is too low. Bromine is open to both objections—it fails to precipitate peptones completely, and at the same time does precipitate some of the amido-acid compounds. While these two sources of error might tend to offset each other under certain conditions, we cannot depend upon such a method for reliable quantitative results.

In our judgment, it is desirable, for best results, to use phosphotungstic acid to separate peptones and amido-acid compounds when the amount of amido-acid compounds is relatively small as compared with peptones, or when they consist mostly of monoamido compounds. This condition occurs in the early stages of cheese ripening, and persists longer in cheese cured at low temperatures ; it occurs also in milk and cheese acted upon by pepsin enzymes, especially in the presence of chloroform.

Tannin-salt solution can be relied upon to give better results than phosphotungstic acid when amido-acid compounds are present in proportions that are relatively large compared with peptones, or when they consist largely of diamido compounds. The former condition prevails in normal cheese cured under usual conditions, especially after the first two weeks of curing.

10. *Determination of Nitrogen in the Form of Ammonia.*

Distil with magnesium oxide 100 c.c. of the filtrate from the tannin-salt precipitation, passing the distillate into a standardised acid, and titrating in the usual way. In our early work the cheese mass itself, suspended in water, was used for distillation, giving slightly higher results than the method just described. The small increase is generally accounted for as coming from the proteids themselves present in the solution. Theoretically it is true that when such bases are present as putrescin and cadaverin they might distil with the ammonia. In one case, where a large quantity of cheese was subjected directly to distillation with magnesium oxide and the distillate examined for these bases, none was found, the distillate consisting entirely of the ammonia salt. The high boiling-points of cadaverin and putrescin, and the consequent difficulty of distilling them with steam, probably accounts for their absence in the distillate.

In our early work on the determination of ammonia in milk and cheese, we subjected to distillation with magnesium oxide and with barium carbonate many different amido compounds, in order to ascertain if any of these bodies when pure could split off basic nitrogen. While some of the products used in our work are not at all likely to be found in cheese or milk, we include them with the others in the list given below. The method was carried out as follows :—Dissolve 1 grm. of each amido body, or if insoluble, suspend it in 50 c.c. of water, and for distillation use 10 c.c. of this mixture diluted to 150 c.c., adding magnesium oxide or barium carbonate, and using ordinary atmospheric pressure.

Amido bodies used were :—

Acetamide.	Diphenylamine.	Phenylenediamine.
Allantoine (*a*).	Glutamic acid.	Trimethylamine.
Arginin.	Glycocol.	Tyrosin.
Aspartic acid.	Histidin.	Uric acid.
Creatin.	Leucin.	Xanthin.
Creatinine.	Lysin.	

(*a*) *Zeit. f. Physiol. Chem.*, 1901, xxxiv., 145.

The result of this work was that nothing was distilled over with either magnesium oxide or barium carbonate in any case except that of trimethylamine, the nitrogen of which was all obtained in the distillate with both reagents.

We have also used the excellent Nencki apparatus, distilling under reduced pressure the filtrate from the tannin-salt precipitation. In comparative trials we have obtained no lower results than when we distil under ordinary atmospheric pressure.

11. *Determination of Nitrogen in the Form of Unsaturated Paracasein Lactate.*

The residue insoluble in water is treated with several portions of a 5 per cent solution of sodium chloride, the process being carried out as in preparing the water extract (see 3, p. 80). The nitrogen in an aliquot part of the 500 c.c. of this salt extract is determined by the Kjeldahl method.

II. Methods for the Separation and Estimation of the Nitrogen Compounds of Milk and their Proteolytic Products.

We will briefly describe the methods used for the separation and estimation of the nitrogen compounds of milk and their proteolytic products in the following order :—

1. Determination of total nitrogen in milk.
2. Determination of nitrogen in the form of casein.
3. Determination of nitrogen in the form of albumin and syntonin.
4. Determination of nitrogen in the form of caseoses.
5. Determination of nitrogen in the form of amido-acid compounds.
6. Determination of nitrogen in the form of peptones.
7. Determination of nitrogen in the form of ammonia.

1. *Determination of Total Nitrogen in Milk.*

Weigh about 5 grms. of milk and determine the nitrogen by the Kjeldahl method.

2. *Determination of Casein.*

To about 10 grms. of milk add 90 c.c. of water at 104° to 108° F. (40° to 42° C.), and then 1·5 c.c. of 10 per cent acetic acid. Agitate and warm at the temperature given above until a flocculent precipitate separates, leaving a clear supernatant liquid. Filter, wash, and treat by the Kjeldahl method for estimating nitrogen.

In fresh milk 2 or 3 c.c. of a saturated solution of alum may be used in place of acetic acid, usually with little higher results. But when the milk casein has been proteolysed to any extent, the use of alum is not permissible, since it precipitates caseoses in addition to casein.

The use of acetic or any other acid in precipitating casein in milk, whose casein has been digested in any degree, precipitates, in addition to casein, any paranuclein that is present. We have not yet succeeded in devising satisfactory methods for the separation of these two compounds.

3. *Determination of Nitrogen in the Form of Albumin and Syntonin.*

The filtrate from 2 is neutralised by caustic alkali, using phenolphthalein as indicator, and is then heated at the temperature of boiling water until the precipitate completely separates and settles. The precipitate is then filtered, washed, and treated by the Kjeldahl method.

4. *Determination of Nitrogen in the Form of Caseoses.*

The filtrate from 3 is heated to 70° C., 1 c.c. of 50 per cent sulphuric acid is added, and then chemically pure zinc sulphate to saturation. Let stand at the temperature indicated until the caseoses completely separate and settle. Then cool the mixture, filter, wash with a saturated solution of zinc sulphate made slightly acid with sulphuric acid, and treat the precipitate by the Kjeldahl method.

5. *Determination of Nitrogen in the Form of Amido-acid Compounds.*

Treat about 50 grms. of milk with a tannin-salt solution or with phosphotungstic acid according to directions given under 8, p. 81.

6. *Determination of Nitrogen in the Form of Peptones.*

From the total nitrogen, subtract that found in all forms other than that of peptones, as indicated under 9, p. 92.

7. *Determination of Nitrogen in the Form of Ammonia.*

See under 10, p. 94.

III. Determination of Chloroform.

When chloroform is used as an antiseptic in milk and cheese it is very essential to know approximately the amount present, in order that we may have a proper control of conditions. We have used the following method successfully :—Place 5 grms. of milk or cheese in a pressure-bottle with about 100 c.c. of alcohol and 5 grms. of caustic potash. The bottle is then heated in an autoclave for half-an-hour at 110° C. The resulting chloride is determined by titration, as for chlorine in sodium chloride.

Recommendation.

It is recommended that the methods presented above be adopted as provisional methods under the head of dairy products.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxix., No. 5.

All the papers in this number have been noticed already in these columns.

No. 6.

Influence of the Nature of the Cathode on the Quantitative Separation of Metals by Electrolysis.—A. Hollard.—Already inserted in full.

A New Method for the Chlorination of the Aromatic Carbides.—A. Seyewetz and M. Biot.—Already noticed.

Chlorination of the Substituted Aromatic Carbides by Plumbico-ammoniacal Chloride.—A. Seyewetz and P. Trawitz.—Already noticed.

A New Di-iodised Phenol.—P. Brenans.—Already noticed.

A New Orthocyclohexanediol and its Derivatives.—Leon Brunel.—Already noticed.

Some Derivatives of Diphenylamine and of the Tolylphenylamines.—F. Reverdin and P. Crépieux.—As a result of their researches on colouring-matters, the authors have succeeded in preparing some derivatives of diphenylamine and of the tolylphenylamines; with the exception of the *o*- and *p*-tolyl-*o'*,-*p'*,-dinitrophenylamines, these derivatives have not yet been described. Nine new derivatives are described, and their analyses given in this paper.

Benzene-*p*-azobenzoic Aldehyde.—P. Freundler.—Already noticed.

Estimation and Organic Analysis of Very Small Quantities of Glycerin.—Maurice Nicloux.—Already inserted in full.

New Reaction of Cystine.—Ali Riza.—According to Benzinger, cystine gives a white precipitate with mercuric chloride, consisting of a combination of these two bodies. However, mercuric chloride does not give a precipitate

directly with cystine; it is necessary, to obtain it by means of this reagent, to reduce the cystine first with tin or zinc and hydrochloric acid. Under these conditions, it decomposes into two molecules of cystein, which then give the above-mentioned white precipitate with the mercuric chloride. By using acid mercuric sulphate, the author has obtained the white precipitate directly from an acid solution of cystine without having recourse to reduction. To effect this, a small quantity of cystine was dissolved in about 1 c.c. of normal sulphuric acid, and an excess of acid mercuric sulphate added; the precipitate appears in a few seconds.

MISCELLANEOUS.

The Iron and Steel Institute.—The following is the corrected list of the papers to be submitted at the forthcoming meeting of the Iron and Steel Institute at Barrow-in-Furness on September 1st to 4th:—

"Alloys of Iron and Tungsten." By R. A. Hadfield, Vice-President.
"The Restoration of Dangerously Crystalline Steel by Heat Treatment." By J. E. Stead, Member of Council, and Arthur W. Richards (Middlesbrough).
"On Sorbitic Steel Rails." By J. E. Stead, Member of Council, and Arthur W. Richards (Middlesbrough).
"Influence of Silicon on Iron." By Thomas Baker, M.Sc. (Sheffield).
"Diffusion of Sulphides through Steel." By Prof. E. D. Campbell (Ann Arbor, Michigan).
"Heat Treatment of Steel." By William Campbell (New York), Carnegie Research Scholar.
"Manufacture of Weldless Steel Pipes." By H. Ehrhardt (Düsseldorf).
"Heat Treatment of Steel Rails high in Manganese." By J. S. Lloyd.
"Regulation of the Combustion in Coke-oven Practice." By D. A. Louis (London).
"Coal as Fuel at Barrow-in-Furness." By W. F. Pettigrew (Barrow-in-Furness).
"On the Diseases of Steel." By C. H. Ridsdale (Middlesbrough).
"The Probability of Iron Ore lying below the Sands of the Duddon Estuary." By J. L. Shaw (Whitehaven).
"Overheating and Burning of Steel." By Prof. A. Stansfield, D.Sc.(Lond.), Assoc.R.S.M. (Montreal), Carnegie Research Scholar.

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2283.

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 86).

Chapter I. (*continued*).

Measurement of the Intensity of Radiation.

The method employed consists in measuring the conductivity acquired by air under the action of radio-active bodies; this method possesses the advantage of being rapid and of furnishing figures which are comparable. The apparatus employed by me for the purpose consists essentially of a plate condenser, A B (Fig. 1). The active

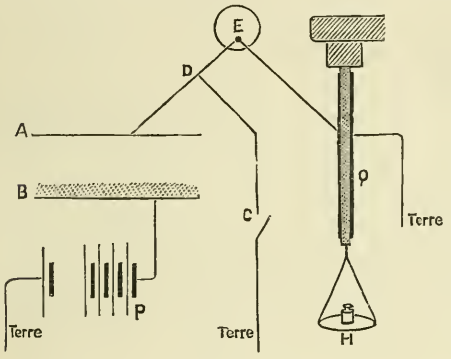

Fig. 1.

body, finely powdered, is spread over the plate B, making the air between the plates a conductor. In order to measure the conductivity, the plate B is raised to a high potential by connecting it with one pole of a battery of small accumulators, P, of which the other pole is connected to earth. The plate A being maintained at the potential of the earth by the connection C D, an electric current is set up between the two plates. The potential of plate A is recorded by an electrometer, E. If the earth connection be broken at C, the plate A becomes charged, and this charge causes a deflection of the electrometer. The velocity of the deflection is proportional to the intensity of the current, and serves to measure the latter.

But a preferable method of measurement is that of compensating the charge on plate A, so as to cause no deflection of the electrometer. The charges in question are extremely weak; they may be compensated by means of a quartz electric balance, Q, one sheath of which is connected to plate A and the other to earth. The quartz lamina is subjected to a known tension, produced by placing weights in a plate, π; the tension is produced progressively, and has the effect of generating progressively a known quantity of electricity during the time observed. The operation can be so regulated that, at each instant, there is compensation between the quantity of electricity that traverses the condenser and that of the opposite kind furnished by the quartz. In this way, the quantity of electricity passing through the condenser for a given time, *i.e.*, the *intensity of the current*, can be measured *in absolute units*. The measurement is independent of the sensitiveness of the electrometer.

In carrying out a certain number of measurements of this kind, it is seen that radio-activity is a phenomenon capable of being measured with a certain accuracy. It varies little with temperature; it is scarcely affected by variations in the temperature of the surroundings; it is not influenced by incandescence of the active substance. The intensity of the current which traverses the condenser increases with the surface of the plates. For a given condenser and a given substance the current increases with the difference of potential between the plates, with the pressure of the gas which fills the condenser, and with the distance of the plates (provided this distance be not too great in comparison with the diameter). In every case, for great differences of potential the current attains a limiting value, which is practically constant. This is the *current of saturation*, or *limiting current*. Similarly, for a certain sufficiently great distance between the plates the current hardly varies any longer with the distance. It is the current obtained under these conditions that was taken as the measure of radio-activity in my researches, the condenser being placed in air at atmospheric pressure.

I append curves which represent the intensity of the current as a function of the field established between the plates for two different plate distances. Plate B was covered with a thin layer of powdered metallic uranium; plate A, connected with the electrometer, was provided with a guard-ring.

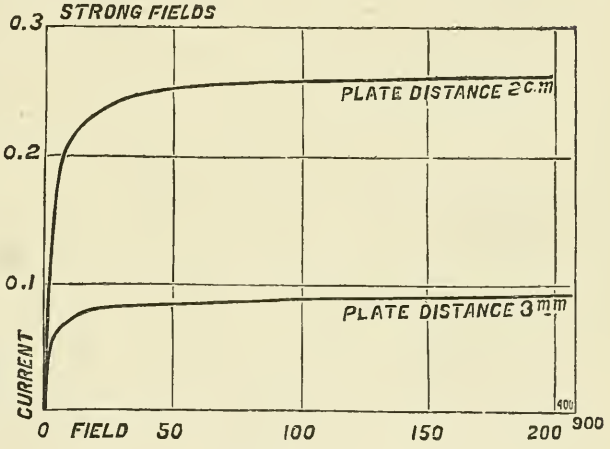

Fig. 2.

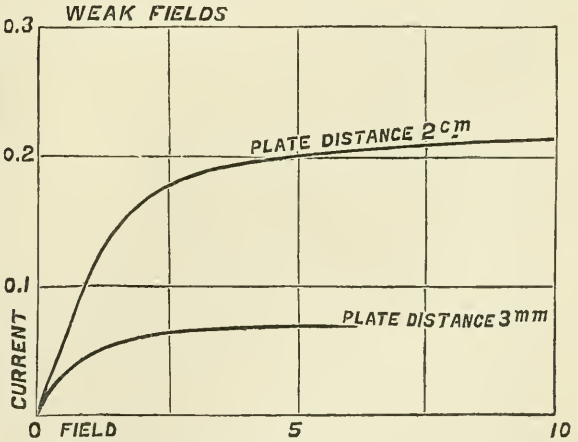

Fig. 3.

Fig. 2 shows that the intensity of the current becomes constant for high potential differences between the plates. Fig. 3 represents the same curves on another scale, and

* Thesis presented to the Faculté des Sciences de Paris.

comprehends only relative results for small differences of potential. At the origin, the curve is rectilinear; the ratio of the intensity of the current to the difference of potential is constant for weak forces, and represents the initial conduction between the plates. Two important characteristic constants of the observed phenomenon are therefore to be recognised :—(1) The *initial conduction* for small differences of potential; (2) the *limiting current* for great potential differences. The limiting current has been adopted as the measure of the radio-activity.

Besides the difference of potential established between the two plates, there exists between them an electromotive force of contact, and these two sources of current combine their effects; for this reason, the absolute value of the intensity of the current changes with the sign of the external difference of potential. In every case, for considerable potential differences, the effect of the electromotive force of contact is negligible, and the intensity of the current is therefore the same whatever be the direction of the field between the plates.

The investigation of the conductivity of air and other gases subjected to the action of Becquerel rays has been undertaken by several physicists. A very complete research upon the subject has been published by Mr. Rutherford.

The laws of the conductivity produced in gases by the Becquerel rays are the same as those found for the Röntgen rays. The mechanics of the phenomenon appear to be the same in both cases. The theory of ionisation of the gases by the action of the Röntgen or Becquerel rays agrees well with the observed facts. This theory will not be put forward here. I will merely record the results to which they point :—

Firstly, the number of ions produced per second in the gas is considered proportional to the energy of radiation absorbed by the gas.

Secondly, in order to obtain the limiting current relatively to a given radiation, it is necessary, on the one hand, to cause complete absorption of this radiation by the gas by employing a sufficient mass of it; on the other hand, it is necessary for the production of the current to use all the ions generated by establishing an electric field of such strength that the number of the ions which recombine may be a negligible fraction of the total number of ions produced in the same time, most of which are carried by the current to the electrodes. The strength of the electric field necessary to give this result is proportional to the amount of ionisation.

According to the recent researches of Mr. Townsend, the phenomenon is more complex when the pressure of the gas is low. At first the current appears to approach to a constant limiting value with increasing difference of potential; but after a certain point has been reached, the current begins again to increase with the field, and with very great rapidity. Mr. Townsend ascribes this increase to a new ionisation produced by the ions themselves when, under the action of the electric field, they acquire a velocity such that a molecule of gas encountering one of them becomes broken down into its constituent ions. A strong electric field and a low pressure are favourable to the production of this ionisation by ions already present, and, as soon as the action is set up, the intensity of the current increases uniformly with the field between the plates. The limiting current could, therefore, only be obtained under conditions of ionisation of which the intensity does not exceed a certain value, and in such a manner that saturation corresponds to fields in which, from multiplicity of ions, ionisation can no longer take place. This condition has occurred in my experiments.

The order of magnitude of the saturation currents obtained with uranium compounds is 10^{-11} ampères for a condenser in which the plates have a diameter of 8 c.m., and are at a distance of 3 c.m. Thorium compounds give rise to currents of the same order of magnitude, and the activity of the oxides of uranium and thorium is very similar.

Radio-activity of the Compounds of Uranium and Thorium.

The following are the figures I obtained with different uranium compounds. I have represented the intensity of the current in ampères by the letter i :—

	$i \times 10^{11}$.
Metallic uranium (containing a little carbon)	2·3
Black oxide of uranium, U_2O_5	2·6
Green ,, ,, U_3O_4	1·8
Hydrated uranic acid	0·6
Uranate of sodium	1·2
,, potassium	1·2
,, ammonium	1·3
Uranium sulphate	0·7
Sulphate of uranium and potassium	0·7
Nitrate of uranium	0·7
Phosphate of copper and uranium	0·9
Oxysulphide of uranium	1·2

The thickness of the layer of the uranium compound used has little effect, provided that the layer is uniform. The following illustrate this point :—

	Thickness of layer. M.m.	$i \times 10^{11}$.
Uranium oxide	0·5	2·7
,, ,,	3·0	3·0
Ammonium uranate	0·5	1·3
,, ,,	3·0	1·4

It may be concluded from this that the absorption of uranium rays by the substance which generates them is very great, since the rays proceeding from deep layers produce no significant effect.

The figures I obtained with thorium compounds enable me to state :—

Firstly, that the thickness of the layer used has considerable effect, especially in the case of the oxide.

Secondly, that the action is only regular if a sufficiently thin layer is used (*e.g.*, 0·25 m.m.). On the contrary, when a thick layer of the substance is used (6 m.m.), the figures obtained vary between two extreme limits, especially in the case of the oxide :—

	Thickness of layer. M.m.	$i \times 10^{11}$.	
Thorium oxide	0·25	2·2	
,, ,,	0·5	2·5	
,, ,,	2·5	4·7	
,, ,,	3·0	5·5	(mean)
,, ,,	6·0	5·5	,,
Thorium sulphate	0·25	0·8	,,

There is here some cause of irregularities which do not exist in the case of the uranium compounds. The figures obtained for a layer of oxide 6 m.m. thick varied between 3·7 and 7·3.

The experiments that I made on the absorption of uranium and thorium rays showed that those of thorium are more penetrating than those of uranium, and that the rays emitted by the oxide of thorium in a thick layer are more penetrating than those emitted by a thin layer of the same. The following figures give the fraction of the radiation transmitted by a sheet of aluminium 0·01 thick :—

Radio-active substance.	Fraction of radiation transmitted by the sheet.
Uranium	0·18
Uranium oxide, U_2O_5	0·20
Uranate of ammonium	0·20
Phosphate of uranium and copper	0·21
Thorium oxide of thickness 0·25 m.m.	0·38
,, ,, 0·5 ,,	0·47
,, ,, 3·0 ,,	0·70
,, ,, 6·0 ,,	0·70
Thorium sulphate 0·25 ,,	0·38

With the uranium compounds, the absorption is the same whatever be the compound used, which leads to the

conclusion that the rays emitted by the different compounds are of the same nature.

The characteristics of the thorium radiation have formed the subject of very complete publications. Mr. Owens has demonstrated that a uniform current is only obtained after some time has elapsed, with an enclosed apparatus, and that the intensity of the current is greatly reduced under the influence of a current of air (which does not occur with the compounds of uranium). Mr. Rutherford has made similar experiments, and has explained them by the proposition that thorium and its compounds produce, besides the Becquerel rays, another *emanation*, composed of extremely minute particles, which remain radio-active for some time after their emission, and are capable of being swept along by a current of air.

The characteristics of the thorium radiation, which have reference to the thickness of the layer employed and to the action of air currents, have an intimate connection with the phenomenon of the *radio-activity induced, and of its propagation from place to place*. This phenomenon was observed for the first time with radium, and will be described later.

The radio-activity of thorium and uranium compounds appears as an *atomic property*. M. Becquerel had already observed that all uranium compounds are active, and had concluded that their activity was due to the presence of the element uranium; he also demonstrated that uranium was more active than its salts. I have investigated, from this point of view, the compounds of thorium and uranium, and have taken a great many measurements of their activity under different conditions. The result of all these determinations shows the radio-activity of these substances to be decidedly an atomic property. It seems to depend upon the presence of atoms of the two elements in question, and is not influenced by any change of physical state or chemical decomposition. The chemical combinations and mixtures containing uranium or thorium are active in proportion to the amount of the metal contained, all inactive material acting as inert bodies and absorbing the radiation.

Is Atomic Radio-activity a general Phenomenon?

As I have said above, I made experiments to discover whether substances other than compounds of uranium and thorium were radio-active. I undertook this research with the idea that it was scarcely probable that radio-activity, considered as an atomic property, should belong to a certain kind of matter to the exclusion of all other. The determinations I made permit me to say that, for chemical elements actually considered as such, including the rarest and most hypothetical, the compounds I investigated were always at least 100 times less active in my apparatus than metallic uranium.

The following is a summary of the substances experimented upon, either as the element or in combination:—

1. All the metals or non-metals easily procurable, and some, more rare, pure products obtained from the collection of M. Etard, at the Ecole de Physique et de Chimie Industrielles de la Ville de Paris.

2. The following rare bodies:—Gallium, germanium, neodymium, praseodymium, niobium, scandium, gadolinium, erbium, samarium, and rubidium (specimens lent by M. Demarçay), yttrium, ytterbium (lent by M. Urbain).

3. A large number of rocks and minerals.

Within the limits of sensitiveness of any apparatus, I ound no simple substance, other than uranium and thorium, possessing atomic radio-activity. It will be suitable to add a few words here concerning phosphorus. White moist phosphorus, placed between the plates of the condenser, causes tbe air between the plates to conduct. However, I do not consider this body radio-active in the same manner as thorium and uranium. For, under these conditions, phosphorus becomes oxidised and emits luminous rays, whilst uranium and thorium compounds are radio-active without showing any chemical change which can be detected by any known means. Further, phosphorus is not active in the red variety, nor in a state of combination.

In a recent work, M. Bloch has demonstrated that phosphorus, undergoing oxidation in air, gives rise to slightly motile ions, which make the air conduct, and cause condensation of aqueous vapour.

Uranium and thorium are elements which possess the highest atomic weights (240 and 232); they occur frequently in the same minerals.

Radio-active Minerals.

I have examined many minerals in my apparatus; certain of them gave evidence of radio-activity, *e.g.*, pitchblende, thorite, orangite, fergusonite, cleveite, chalcolite, autunite, monazite, &c. The following is a table giving in ampères the intensity, *i*, of the current obtained with metallic uranium and with different minerals:—

	$i \times 10^{11}$.
Uranium	2·3
Pitchblende from Johanngeorgenstadt	8·3
" " Joachimsthal	7·0
" " Pzibran	6·5
" " Cornwallis	1·6
Cleveite	1·4
Chalcolite	5·2
Autunite	2·7
Various thorites	0·1, 0·3, 0·7, 1·3, 1·4
Orangite	2·0
Monazite	0·5
Xenotime	0·03
Æschynite	0·7
Fergusonite (two samples)	0·4, 0·1
Samarskite	1·1
Niobite (two samples)	0·1, 0·3
Tantalite	0·02
Carnotite	6·2

The current obtained with orangite (native oxide of thorium) varied greatly with the thickness of the layer. By increasing this thickness from 0·25 m.m. to 6 m.m. the current increased from 1·8 to 2·3.

All the minerals which showed radio-activity contained uranium or thorium; their activity is therefore not surprising, but the intensity of the action in certain cases is unexpected. Thus pitchblendes (ores of uranium oxide) are found which are four times as active as metallic uranium. Chalcolite (double phosphate of copper and uranium) is twice as active as uranium. Autunite (phosphate of uranium and calcium) is as active as uranium. These facts did not accord with previous conclusions, according to which no mineral should be so active as thorium or uranium.

To throw light on this point, I prepared artificial chalcolite by the process of Debray, starting with the pure products. The process consists in mixing a solution of uranium nitrate with a solution of copper phosphate in phosphoric acid and warming to 50° or 60°. After some time, crystals of chalcolite appear in the liquid.

Chalcolite thus obtained possesses a perfectly normal activity, given by its composition; it is two and a-half times less active than uranium.

It therefore appeared probable that if pitchblende, chalcolite, and autunite possess so great a degree of activity, these substances contain a small quantity of a strongly radio-active body, differing from uranium and thorium and the simple bodies actually known. I thought that if this were indeed the case, I might hope to extract this substance from the ore by the ordinary methods of chemical analysis.

(To be continued).

EXPERIMENTS IN RADIO-ACTIVITY, AND THE PRODUCTION OF HELIUM FROM RADIUM.*

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.,
and
FREDERICK SODDY, M.A.

1. *Experiments on the Radio-activity of the Inert Gases of the Atmosphere.*

Of recent years many investigations have been made by Elster and Geitel, Wilson, Strutt, Rutherford, Cooke, Allen, and others, on the spontaneous ionisation of the gases of the atmosphere, and on the excited radio-activity obtainable from it. It became of interest to ascertain whether the inert monatomic gases of the atmosphere bear any share in these phenomena. For this purpose a small electroscope contained in a glass tube of about 20 c.c. capacity, covered in the interior with tin-foil, was employed. After charging, the apparatus, if exhausted, retained its charge for thirty-six hours without diminution. Admission of air caused a slow discharge. In similar experiments with helium, neon, argon, krypton, and xenon, the last mixed with oxygen, the rate of discharge was proportional to the density and pressure of the gas. This shows that the gases have no special radio-activity of their own, and accords with the explanation already advanced by these investigators, that the discharging power of the air is caused by extraneous radio-activity.

Experiments were also made with the dregs left after liquefied air had nearly entirely evaporated, and again with the same result; no increase in discharging power is produced by concentration of a possible radio-active constituent of the atmosphere.

2. *Experiments on the Nature of the Radio-active Emanation from Radium.*

The word emanation originally used by Boyle ("substantial emanations from the celestial bodies") was resuscitated by Rutherford to designate definite substances of a gaseous nature, continuously produced from other substances. The term was also used by Russell ("emanation from hydrogen peroxide") in much the same sense. If the adjective "radio-active" be added, the phenomenon of Rutherford is distinguished from the phenomena observed by Russell. In this section we are dealing with the emanation, or radio-active gas obtained from radium. Rutherford and Soddy investigated the chemical nature of the thorium emanation (*Phil. Mag.*, 1902, p. 580), and of the radium emanation (*Phil. Mag.*, 1903, p. 457), and came to the conclusion that these emanations are inert gases which withstand the action of reagents in a manner hitherto unobserved, except with the members of the argon family. This conclusion was arrived at because the emanations from thorium and radium could be passed without alteration over platinum and palladium black, chromate of lead, zinc dust, and magnesium powder, all at a red heat.

We have since found that the radium emanation withstands prolonged sparking with oxygen over alkali, and also, during several hours, the action of a heated mixture of magnesium powder and lime. The discharging power was maintained unaltered after this treatment, and inasmuch as a considerable amount of radium was employed, it was possible to use the self-luminosity of the gas as an optical demonstration of its persistence.

In an experiment in which the emanation mixed with oxygen had been sparked for several hours over alkali, a minute fraction of the total mixture was found to discharge an electroscope almost instantly. From the main quantity of the gas, the oxygen was withdrawn by ignited phosphorus, and no visible residue was left. When, however, another gas was introduced, so as to come into contact with the top of the tube, and then withdrawn, the emanation was found to be present in it in unaltered amount. It appears, therefore, that phosphorus burning in oxygen and sparking with oxygen have no effect upon the gas so ar as can be detected by its radio-active properties.

The experiments with magnesium-lime were more strictly quantitative. The method of testing the gas before and after treatment with the reagent was to take 1/2000 part of the whole mixed with air, and after introducing it into the reservoir of an electroscope to measure the rate of discharge. The magnesium-lime tube glowed brightly when the mixture of emanation and air was admitted, and it was maintained at a red heat for three hours. The gas was then washed out with a little hydrogen, diluted with air and tested as before. It was found that the discharging power of the gas had been quite unaltered by this treatment.

The emanation can be dealt with as a gas; it can be extracted by aid of a Töpler pump; it can be condensed in a U-tube surrounded by liquid air, and when condensed it can be "washed" with another gas, which can be pumped off completely, and which then possesses no luminosity and practically no discharging power. The passage of the emanation from place to place through glass tubes can be followed by the eye in a darkened room. On opening a stopcock between a tube containing the emanation and the pump, the slow flow through the capillary tube can be noticed; the rapid passage along the wider tubes, the delay caused by the plug of phosphorus pentoxide, and the sudden diffusion into the reservoir of the pump. When compressed, the luminosity increased, and when the small bubble was expelled through the capillary it was exceedingly luminous. The peculiarities of the excited activity left behind on the glass by the emanation could also be well observed. When the emanation had been left a short time in contact with the glass, the excited activity lasts only for a short time; but after the emanation has been stored a long time the excited activity decays more slowly.

The emanation causes chemical change in a similar manner to the salts of radium themselves. The emanation pumped off from 50 m.grms. of radium bromide after dissolving in water, when stored with oxygen in a small glass tube over mercury, turns the glass distinctly violet in a single night; if moist, the mercury becomes covered with a film of the red oxide, but if dry, it appears to remain unattacked. A mixture of the emanation with oxygen produces carbon dioxide when passed through a lubricated stopcock.

3. *Occurrence of Helium in the Gases Evolved from Radium Bromide.*

The gas evolved from 20 m.grms. of pure radium bromide (which we are informed had been prepared three months) by its solution in water, and which consisted mainly of hydrogen and oxygen (*cf.* Giesel, *Ber.*, 1903, 347) was tested for helium, the hydrogen and oxygen being removed by contact with a red-hot spiral of copper wire, partially oxidised, and the resulting water vapour by a tube of phosphorus pentoxide. The gas issued into a small vacuum tube which showed the spectrum of carbon dioxide. The vacuum tube was in train with a small U-tube, and the latter was then cooled with liquid air. This much reduced the brilliancy of the CO_2 spectrum, and the D_3 line of helium appeared. The coincidence was confirmed by throwing the spectrum of helium into the spectroscope through the comparison prism, and shown to be at least within 0·5 of an Angström unit.

The experiment was carefully repeated in apparatus constructed of previously unused glass with 30 m.grms. of radium bromide, probably four or five months old, kindly lent us by Prof. Rutherford. The gases evolved were passed through a cooled U-tube on their way to the vacuum tube, which completely prevented the passage of carbon dioxide and the emanation. The spectrum of helium was obtained, and practically all the lines were seen, including those at 6677, 5876, 5016, 4932, 4713, and 4472. There were also present three lines of approximate wave-lengths, 6180, 5695, 5455, that have not yet been identified.

On two subsequent occasions, the gases evolved from both solutions of radium bromide were mixed, after four days' accumulation, which amounted to about 2·5 c.c. in

* A Paper communicated to the Royal Society, July 28, 1903.

each case, and were examined in a similar way. The D_3 line of helium could not be detected. It may be well to state the composition found for the gases continuously generated by a solution of radium, for it seemed likely that the large excess of hydrogen over the composition required to form water, shown in the analysis given by Bödlander (*Ber., loc. cit.*) might be due to the greater solubility of the oxygen. In our analyses the gases were extracted with the pump, and the first gave 28·6, the second 29·2 per cent of oxygen. The slight excess of hydrogen is doubtless due to the action of the oxygen on the grease of the stopcocks, which has been already mentioned. The rate of production of these gases is about 0·5 c.c. per day for 50 m.grms. of radium bromide, which is over twice as great as that found by Bödlander.

4. *Production of Helium by the Radium Emanation.*

The maximum amount of the emanation obtained from 50 m.grms. of radium bromide was conveyed by means of oxygen into a U-tube cooled in liquid air, and the latter was then extracted by the pump. It was then washed out with a little fresh oxygen, which was again pumped off. The vacuum tube sealed on to the U-tube, after removing the liquid air, showed no trace of helium. The spectrum was apparently a new one, probably that of the emanation, but this has not yet been completely examined, and we hope to publish further details shortly. After standing from the 17th to the 21st inst., the helium spectrum appeared, and the characteristic lines were observed identical in position with those of a helium tube thrown into the field of vision at the same time. On the 22nd, the yellow, the green, the two blues, and the violet, were seen, and in addition the three new lines also present in the helium obtained from radium. A confirmatory experiment gave identical results.

We wish to express our indebtedness to the Research Fund of the Chemical Society for a part of the radium used in this investigation.

ON THE

INTENSELY PENETRATING RAYS OF RADIUM.*

By Hon. R. J. STRUTT, Fellow of Trinity College, Cambridge.

Radium is known to emit three types of radiation. These are—

1. The α-rays, very easily absorbed by solids, and carrying a positive electric charge.
2. The β-rays, more penetrating than these, and negatively charged.
3. The γ-rays, intensely penetrating, and not conveying an electric charge at all.

In a paper published in the *Phil. Trans.* for 1901, I investigated the relative ionisations of gases by the α- and β-rays. The present communication may be regarded as a sequel to that one, and deals with the γ-rays.

The radium employed was of activity 1000 (uranium = 1), and was contained in a glass cell, over which was cemented a piece of thin aluminium. The cell was placed in a cavity in a cavity in a block of lead, and over it was placed a disc of lead 1 c.m. in thickness. This it was considered would suffice to suppress all but the γ-rays, which are much the most penetrating.

In measuring the electrical leakage, the electroscope method was employed. The apparatus was that described in a paper published in the *Philosophical Magazine* for June, 1903, p. 681.

The radium, covered by the thick lead, was placed under the apparatus, and the rate of leak determined when the different gases filled the testing vessel.

The conditions were, of course, arranged so as to use a saturating E.M.F. The γ-rays are so penetrating that there can be no question of their being appreciably absorbed in a moderate thickness of gas.

* A Paper communicated to the Royal Society, August 5, 1903.

For the methods of preparation of the gases I must refer to the former paper (*Phil. Trans.*, A., 1901, vol. cxcvi., p. 508).

The results were as follows; the rates of leak are given in scale divisions per hour, and are corrected to 30 inches pressure :—

Gas.	Rate of leak.	Mean.
Hydrogen	10·4, 10·5, 10·4, 11·2, 10·4, 11·2, 9·86, 10·1, 10·2 ..	10·5
Air	65·2, 66·6, 66·6, 60·0, 57·0, 61·5, 60·2, 63·0, 58·2, 58·3, 56·6, 56·2	62·1
Oxygen	75·0, 74·2, 71·0, 74·1 . ..	73·6
Carbon dioxide . ..	96·0, 95·4, 94·5, 95·1, 94·1, 94·7	95·0
Cyanogen	107, 104, 106, 106	106·0
Sulphur dioxide . ..	132, 126, 134, 135	132·0
Chloroform	297, 298, 290, 327	303·0
Methyl iodide	298, 292, 310, 291	298·0
Carbon tetrachloride .	363, 351, 344, 349	352·0

The following table gives the relative ionisations, referred to air as unity. The values of the same constants for the α- and β-rays formerly found are included, and also measurements of relative ionisation under Röntgen rays. These latter form part of an investigation not hitherto published :—

Relative Ionisations.

Gas.	Relative density.	Relative ionisation.			
		α-Rays.	β-Rays.	γ-Rays.	Röntgen rays.
Hydrogen ..	0·0693	0·226	0·157	0·169	0·114
Air	1·00	1·00	1·00	1·00	1·00
Oxygen	1·11	1·16	1·21	1·17	1·39
Carbon dioxide	1·53	1·54	1·57	1·53	1·60
Cyanogen ..	1·86	1·94	1·86	1·71	1·05
Sulphur dioxide	2·19	2·04	2·31	2·13	7·97
Chloroform ..	4·32	4·44	4·89	4·88	31·9
Methyl iodide .	5·05	3·51	5·18	4·80	72·0
Carbon tetrachloride ..	5·31	5·34	5·83	5·67	45·3

The determinations for the γ-rays are less accurate than the former ones for the α- and β-rays, on account of the very much smaller rates of leak which have to be measured. I think, if this be taken into account, there is no reason to doubt that, within the limits of experimental error, the γ-rays give the same values as the β-rays. These values are nearly proportional to the density of the gas, except in the case of hydrogen. The law which holds in the case of Röntgen rays is totally different.

This conclusion throws some light on the nature of the γ-rays. The view seems to be gaining ground that these are Röntgen rays, produced by the impact of the β-rays on the radium itself (see, for instance, Mdme. Curie, "Thèses presentées à la Faculté des Sciences," 1903, p. 83; Chem. News, vol. lxxxviii., p. 85 *et seq*). This theory seems to have much to recommend it. The β rays should, by analogy with the cathode rays in a vacuum tube, produc Röntgen rays when they strike a solid obstacle, and these Röntgen rays should be much more penetrating than the β-rays themselves. The γ-rays seem at first sight to be just what should be expected. But the present paper shows that, in one respect at all events, the γ-rays behave quite differently to Röntgen rays, while, on the other hand, they resemble the α- and β-rays. There seems to be a possibility that they, too, are of a corpuscular nature, though uncharged with electricity. This would account for the absence of magnetic deflection.

I do not think that the absence of conspicuous Röntgen radiation is very hard to understand, if we consider tha the current emitted in cathode rays by a square inch of intensely active radium is only 10^{-11} ampères; the current through a focus tube is of the order 10^{-2} ampères, and probably a great part of this is carried by the cathode rays.

ELECTROLYTIC APPARATUS.*

By F. MOLLWO PERKIN, Ph.D.

Owing to the great expense of platinum and the necessity for its use in electro-chemical analysis, members may be interested in the description of a simple form of electrode, which is comparatively inexpensive and is very satisfactory.

In Fig. 1, which shows the electrodes, the cathode is in the form of a flag, and is made of platinum gauze, which is held rigid by means of a platino-iridium frame (10 per cent iridium); the frame, which is roughened by means of the sand-blast, has a stout piece of iridio-platinum wire welded on to it. The wire, of course, is for holding the electrode in position during analysis. The loop near the top of the wire is for hanging the electrode on the balance. The anode is made of iridio-platinum wire, and is bent upon itself in such a way that when it is placed into position for electrolysis, as illustrated in Fig. 2, an even current density is obtained on all parts of the cathode. The distance between the two sides of the anode is 2·5 c.m., therefore when in position it is 1·25 c.m. distant from each side of the cathode.

The cathode is 6 c.m. high and 4·3 c.m. wide, and the length of the supporting wire is 7·5 c.m., the loop being 2·5 c.m. from the end. As the anode is opposed to both sides of the cathode during electrolysis, it follows from the above measurements that the total cathode surface is 50·4 c.m.^{2}, that is practically half a square decimetre, which, as the C.D. for analytical purposes is generally calculated per square decimetre of surface, is a very convenient size. It is not essential for the cathode to be made of gauze—in many cases sheet platinum is quite as useful; but for metallic deposits which are inclined to exfoliate, such as bismuth and antimony, the gauze is more satisfactory: it is also very useful for mercury and for peroxide deposits. The gauze should not be too fine; the finest which I have found satisfactory is about 50 to 60 meshes to the square

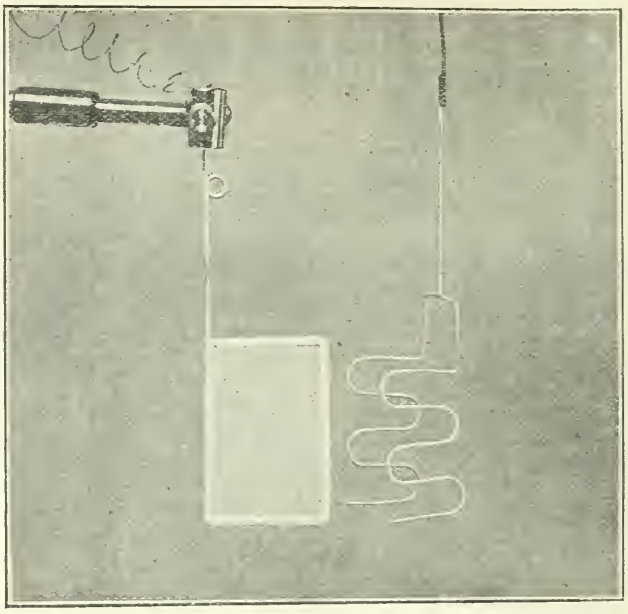

Fig. 1.

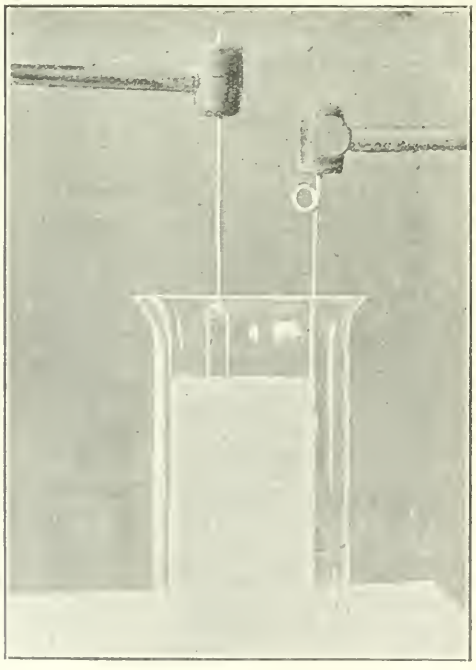

Fig. 2.

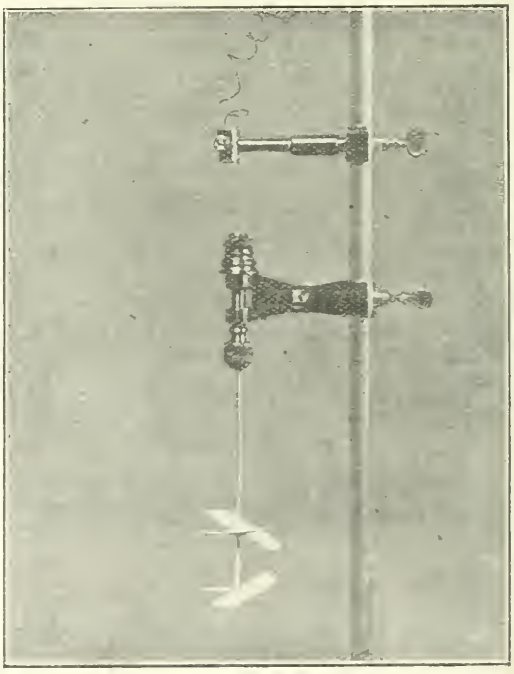

Fig. 3.

* A Paper read before the Faraday Society, June 30, 1903.

centimetre. When it is too fine there is a tendency for hydrogen to collect upon the surface and thus cause polarisation.

The weight of the cathode, when made of platinum sheet, is about 14·5 grms. If thinner platinum is employed the weight can be reduced to 8 grms., but I have found it better not to make them of very thin platinum, because then they are fragile, and there is a tendency for the deposits not to adhere well at the edges. The weight of the gauze electrode is about 15 grms. It follows that, as these electrodes weigh much less than the basin or cylinder ones, they are much cheaper. A basin usually weighs from 45 to 60 grms., and a cylinder from 26 to 28 grms.

These electrodes are also more satisfactory for carrying out electrolytic separations, the manipulation being much easier than with the basin. Suppose, *e.g.*, that one is electrolysing a mixture of copper and iron salts. In the first place the copper would be deposited out from an acid solution ; then, after neutralising, the iron would be electrolysed out. Now when a basin is used, the solution has to be transferred to a beaker, and, as the manipulation has to be rapid, there is a danger of loss through spilling ; further, the acid solution must not be left in contact with the copper deposit. The dish therefore must be washed at once, and the solution which is clinging to its sides, and which contains iron, is lost. In the case of the flag electrode, the cathode is rapidly raised out of the beaker and the solution at once washed off its sides, while it is hanging over the top of the beaker, by means of a wash-bottle. The solution in the beaker can then be neutralised without being transferred to another vessel ; multiplication of manipulation is thus avoided.

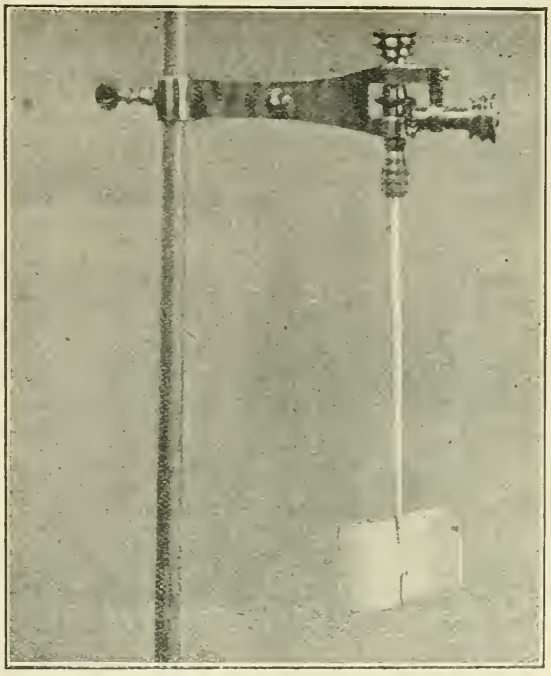

Fig. 4.

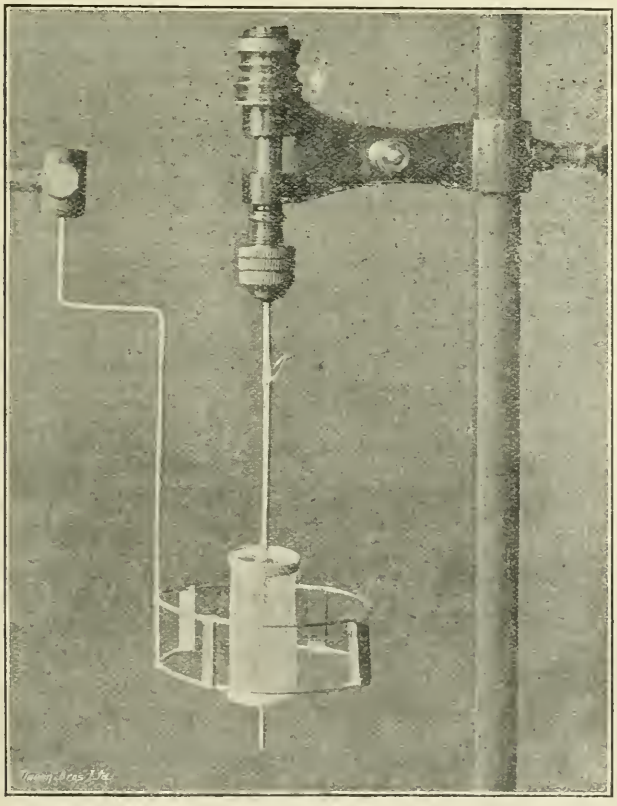

Fig. 5.

Apparatus for Rotating Electrodes.

It is often necessary in electrolysis to keep the electrolyte agitated. This is generally done by means of an agitator, entirely separated from the electrodes and rotated by means of a water-turbine or motor. In many cases, however, much better results are obtained if one of the electrodes is itself caused to rotate. In most of the descriptions of rotating electrodes, there seems to have been considerable difficulty in obtaining good electrical contact, and the methods employed have often been rather complicated. Fig. 3 shows an arrangement which has been found to work extremely well.

It consists of a supporting arm, made of gun-metal, the end of which is drilled to allow a spindle to pass. This spindle carries a small chuck (such as is used for fixing small drills on a lathe) which is used for fixing the rotator. The grooved pulley, which is fastened on to the upper end of the spindle, bears on the top of the arm, which is ground smooth. The whole arrangement is driven by means of a belt from a water-turbine or electrical motor. This arrangement is found to give very perfect contact and to work with very little friction. The parts should only be slightly lubricated, the best lubricant being a mixture of graphite and vaseline. The water-turbine, which has proved very useful and has been working for a long time, has ball bearings—an unusual nicety—and was obtained from Messrs. Baird and Tatlock, Glasgow.

Fig. 4 shows another form of the rotator, which can be driven either from a horizontal or vertical pulley, and is also convenient for working several apparatus in series. The electrode shown in Fig. 3 is of iridio-platinum, and has been used with very satisfactory results in the electrical

oxidation of organic substances. The electrode in Fig. 4 is of aluminium.

I have found the following method work very well for making rotating lead electrodes. Thin lead pipe, to which the vanes for mixing the liquid are burned, is drawn over a steel rod of the same diameter as the bore of the pipe. The steel rod protrudes about an inch above the top of the pipe, in order that it may be fastened in the chuck. The pipe is burned at the bottom and the top to prevent the solution from running in between it and the steel core. If a central core such as this is not used, lead electrodes are not sufficiently rigid to use for rotating purposes.

Rotating Cathode for Analysis.

In Fig. 5 is shown a rotating cathode and a stationary anode for electrolytic depositions. It is found that the rate of deposition of a metal from its solutions is very much accelerated and that a higher C.D. can be employed when the cathode is kept in rapid motion. The cathode is a small cylinder of platinum gauze which has a combined surface of about 25 c.m.^{2}. The anode B is in the form of a double circle of stout platinum wire, and has four little baffles placed at intervals round it to prevent the liquid from rotating with the cathode. Of course, for peroxide deposits the rotating electrode would be the anode. A cylinder of sheet platinum also gives very good results, but in this case very little metal is deposited upon the inner surface. Longitudinal slits, however, partially get over this difficulty, but with gauze as shown in the figure the deposition is practically equal inside and outside.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month ending July 31st, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Charles Perrin, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, August 10th, 1903.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 218 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 218 samples examined by us during the month, 216 were found to be clear, bright, and well filtered; and two samples were recorded as slightly turbid.

The rainfall at Oxford during July, though above the average, is considerably less than that recorded during June. The actual fall has been 3·47 inches; the average for the month is 2·49 inches; this gives an excess of 0·98 inch, which, added to the previous one of 7·83 inches, makes a total excess for the year of 8·81 inches, which is 66·2 per cent above the thirty-five years' average.

The results of the chemical examination of the London waters during the month of July show that the soluble organic matter in the average supply has considerably diminished, and that the general character of the unfiltered Thames water is now approaching that which is generally typical of its composition during the summer months.

Our bacteriological examinations of 387 samples taken during the last month have given the results recorded in the following table. Besides these samples we have examined 317 others from special wells, standpipes, &c., making a total of 704 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	258
New River, filtered (mean of 81 samples) ..	11
Thames, unfiltered (mean of 27 samples)	3805
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 200 samples)	23
Ditto ditto .. .. highest	250
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 27 samples) ..	261
River Lea, from the East London Water Company's clear-water wells (mean of 26 samples)	36

Of the 307 daily samples taken from the filter wells of the Metropolitan Water Companies, nineteen, or 6·1 per cent, were sterile. There were ten samples, or 3·2 per cent, containing more than 100 microbes, and of these, four samples contained more than 150 microbes per c.c. The ten excess samples contained an average of 159 microbes per c.c.: in June fifteen excess samples contained an average of 247 microbes per c.c. The above results show a great improvement in the bacteriological quality of the water during the past month. The natural unfiltered Thames water has improved bacteriologically about 50 per cent, and the supply may now be said to be approaching its normal summer condition.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

LIQUID BATHS FOR MELTING-POINT DETERMINATIONS.

By HEYWARD SCUDDER.

A mixture prepared by boiling together for five minutes seven parts by weight of sulphuric acid (sp. gr. 1·84) and three parts by weight of potassium sulphate remains a transparent liquid at ordinary temperatures, and can be heated up to 325° without boiling. If the proportions are changed to six parts by weight of acid and four parts of the sulphate, the mixture forms a soft mass at ordinary temperatures (though after boiling and then cooling down it will usually remain liquid for half-an-hour or more) melting from 60—100° and boiling above 365°. Acid potassium sulphate can be used instead of potassium sulphate. In this case the amount should be calculated to give the same ratio of potassium sulphate to sulphuric acid.

These mixtures are self-clearing, and remain permanently white (turning slightly yellowish at about 230°) unless much organic matter gets in. They can be cleared, if brown, by boiling with a few drops of concentrated nitric acid or with a small crystal of potassium nitrate. The vapour is so slightly acid that the capillary can always be fastened to the thermometer by a rubber band, provided the band is 1 to 2 c.m. above the surface of the bath. Platinum wire need never be used. In preparing the bath, after the potassium sulphate has melted the two layers should be mixed, or explosive boiling may occur.

Most melting-points given accurately are below 325°. The first mixture is therefore suitable for all ordinary purposes. It does not have to be renewed frequently as does the ordinary sulphuric acid bath, nor does it become per-

manently discoloured as does paraffin after short use, even though prepared by distillation under diminished pressure.

If the bath has solidified (which happens sometimes under unknown conditions, though very rarely), boiling for for a minute or two will bring it back to its original condition. If it has not been used for a number of weeks, it should be boiled for a minute or two before using for temperatures above 300°.

For temperatures from 360° to 600° Mr. Booth, working under the direction of Dr. Mulliken of this laboratory, has found that the most satisfactory bath is fused zinc chloride. This melts to a clear transparent liquid at about 250°. After use it must be poured out on a tile while liquid, since it expands on solidification, and will crack any flask or beaker in which it is allowed to grow cold. It can be cleared from organic impurities by heating with a small crystal of potassium nitrate. Unless the zinc chloride used is pure, the bath will gradually become opaque after a short time, and cannot be made transparent again.

The temperatures given here are uncorrected. They were obtained in a melting-point apparatus made by inserting a test-tube in a round-bottom flask (150—250 c.c.). The bottom of the tube is about 1 c.m. from the bottom of the flask. The bath is placed both in the test-tube and in the flask. In this apparatus fresh sulphuric acid (sp. gr. 1·84) can be used up to 280—300°. In using the sulphate mixtures, if the upper part of the tube becomes cloudy from a film of solid, it can be cleared by boiling with a little concentrated nitric acid. In using such an apparatus it is not safe to heat it much above the temperatures given here for the various baths, since the boiling is apt to start very violently. It is safe to heat it till large bubbles begin to rise moderately frequently.

When these baths are used in open beakers, it is not possible with sulphuric acid or the sulphate mixtures to obtain temperatures as high as those previously mentioned, without having disagreeable amounts of acid vapour given off. The zinc chloride bath can be used in a beaker up to about 600°.

The sulphate mixtures seem to contain some compound in a persistent state of supersaturation. Although possessed of considerable oxidising power when hot, it is a curious fact that they are markedly less caustic than hot concentrated sulphuric acid when dropped on the skin.—*Journal of the American Chemical Society*, xxv., No. 2.

THE NATIONAL PHYSICAL LABORATORY.

Report by the Director on the Work in the Engineering and Physics Departments during the Half Year ended June 30, 1903.

The following statement was prepared by the Director, and laid before the Executive Committee at their Meeting on July 17th, as an interim report on the research work in progress.

The Committee, believing it would be of interest to a wider circle, ordered it to be printed and circulated.

Engineering Laboratory.

In the wind pressure research the case of flat surfaces exposed to a perpendicular current of air has been fully worked out, and a general relation established which is now being tested for the case of larger surfaces exposed to the natural wind. The case of parallel plates at varying distances apart has been treated, and experiments are also in progress on the pressure on inclined surfaces. Dr. Stanton hopes to have a paper on the results obtained at present ready for publication very shortly.

The Testing Machine for alternating stresses is nearing completion, and will, it is hoped, be ready for working in the Autumn.

Drawings have been prepared and some preliminary tests made for the research into the constants of steam.

Thermometry.

Dr. Harker has continued his comparison between the air thermometer, the platinum thermometer, and the thermo-junctions, and the work is now complete for temperatures between 0° C. and about 1050° C. The first part of the work for temperatures up to 500° C. was done with M. Chappuis, at Sèvres, and the results have been published. Dr. Harker is now preparing for publication results up to temperatures of 1050° C. obtained at Bushy.

He has also constructed and subjected to stringent tests a set of platinum thermometers for the British Association.

A small research on the specific heat of iron at high temperatures—700° C. to 1000° C.—is nearly complete and promises to be of interest.

Electricity.

Mr. F. E. Smith's research on the resistance of mercury and the construction of a standard mercury resistance is practically complete. Some 10 or 12 tubes have been calibrated, and give results which will only differ among themselves by some few parts in 100,000. The value of the specific resistance of mercury will probably prove to be very close to that determined by myself and Mr. Fitzpatrick in 1888. On the assumption that the absolute value of the wire standards in the Laboratory is known, the length of the column of mercury, 1 sq. m.m. in section, having a resistance of 10^9 C.G.S. units is found to be almost exactly 106·29 c.m.

The difference between Mr. Smith's results and those of the Reichanstalt will not be more than some few parts in 100,000.

Mr. Smith has also made good progress with a research into some of the anomalies of the Clark Cell.

An investigation of some importance into the changes in insulating strength of various dielectrics, used in motors, transformers, &c., due to continued heating, by Mr. A. Campbell and Mr. Rayner, undertaken for the Engineering Standards Committee, promises to lead to results of value.

Metallurgy.

In the Metallurgical Division preparations have been made for the work on Nickel Steel in conjunction with Mr. Hadfield; the material is being prepared by him.

Meanwhile, considerable advance has been made with a series of determinations on some iron carbon alloys.

The solidifying points and cooling curves of a series of pure iron carbon alloys have been determined, using platinum platinum-iridium and platinum platinum-rhodium thermojunctions. The range of carbon is from 0·15 to 3·55 per cent; the range of temperature from 1502° C. to 1111° C. on the thermojunction scale. About 15 alloys have been made, the weight of each being about 4 lbs.

The ingots have been analysed for carbon, sulphur, and silicon. The percentages of the two last named elements do not increase during the time needed for melting. Further, the ingots are satisfactorily homogeneous in composition.

The apparatus for taking cooling curves by the differential method is in working order, and the above mentioned alloys will be examined in this way.

The Director hopes that a number of important results may be published during the Autumn.

The equipment of the photometric room is approaching completion. The main photometer bench which is being standardised at the Reichanstalt has not yet been delivered.

On its arrival the Director hopes to issue a special circular giving an account of the equipment and a statement as to the conditions of the tests and the fees.

Regulations for the Examination of Lister-Gerber and other Similar Milk Testing Apparatus.

The Commitee of the National Physical Laboratory are prepared to receive, for the purpose of verification, the pipettes, measuring glasses, and test bottles used in the Lister-Gerber and other similar methods of testing milk.

The apparatus to be tested should be sent securely packed to the Director, the National Physical Laboratory, Bushy House, Teddington. The carriage to and fro must be paid by the sender. A letter of advice, which should contain the maker's name, a description of the instruments sent, and full directions for their return, must accompany all instruments sent for verification.

The Laboratory Authorities insure against damage from fire, theft, or accident, apparatus while in their custody. They also insure against risks of transit to and from the Laboratory, apparatus sent to them for testing. They will not, however, be responsible for a sum exceeding £100 on any one instrument unless a letter has been received and acknowledged by them before the instrument is sent, advising that the instrument is being sent, and requesting them to insure it for some definite sum. The value for which goods are insured is the cost price of manufacture. In all cases, a sum sufficient to cover the cost of insurance will be charged with the fees.

Limits of Accuracy.

Milk Test Bottles.—Butter and Cheese Test Bottles.—Test Bottles for Estimating the Water in Butter.

The bottles will be tested at five points on the stem graduations, and will receive the Laboratory stamp, provided—

i. That the error at no point is more than 0·006 c.c.
ii. That the difference between the errors at any two points tested is not greater than 0·006 c.c.

Pipettes for delivering Sulphuric Acid of Specific Gravity 1·820—1·825 at 15° C.

Capacity of pipette.	Time of delivery of acid.	Permissible error.
6·5 c.c.	At least 20 seconds	0·05 c.c.
10 c.c.	,, ,,	0·1 c.c.

Water Pipettes.

Capacity of pipette.	Time of delivery of water.	Permissible error.
8·2 c.c.	At least 30 seconds	0·02 c.c.
12 c.c.	,, ,,	0·03 c.c.
10 c.c. divided into $\frac{1}{10}$ c.c.	At least 30 seconds for 10 c.c. . ..	Permissible error at any point is 0·02 c.c. The difference between the errors at any two points must not be greater than 0·02 c.c.

Amyl Alcohol Pipette.

Capacity.	Time of delivery.	Permissible error.
1 c.c.	At least 20 seconds	0·01 c.c.

Milk Pipette.

11 c.c.	At least 30 seconds	0·03 c.c.

Cream Pipette.

3 c.c.	At least 20 seconds	0·03 c.c.

Graduated Measuring Glasses.

These will be tested at five points.

General Conditions.

Vessels to be tested should be marked *permanently* with :—

i. The capacity.
ii. The temperature at which the capacity corresponds to the mark.
iii. A letter or letters to indicate the purpose for which they are to be used, *e.g.*, pipettes should bear a letter indicative of the liquid they are intended to deliver. The abbreviations suggested are :—

A. for acid.
A.A. for amyl alcohol.
Cr. for cream.
M. for milk.
W. for water.

Attention should be paid to the following points :—

i. The cross section of that part of a vessel on which a mark is made should be circular.
ii. Marks must be fine, and only drawn upon cylindrical or regularly formed parts.
iii. The smallest distance apart of two neighbouring marks must not be less than 1 m.m.
iv. Marks should be sufficiently long to permit of accurate measurement.
v. Vessels should be sent clean. This is ensured by first cleaning them mechanically as far as possible, next treating them with a mixture of potassium bichromate and sulphuric acid in the cold, and, lastly, rinsing them thoroughly with distilled water. An extra fee is charged if it is necessary to clean a vessel.

Stamping of Vessels Tested.

Vessels which pass the test will receive the Laboratory monogram :—

№ (M).

It must be clearly understood that where a pipette is stamped as correct this holds solely for the liquid it is intended to deliver, and no other. The letter (**M**) after the Laboratory monogram indicates that the certificate is applicable only to vessels used for milk, butter, and cream tests.

Fees.

	£	s.	d.
Test bottles, tested at five points.. ..	0	0	6
Pipettes with one mark	0	0	6
Measuring glasses with one mark.. ..	0	0	9
Graduated pipettes, tested at five points	0	1	6
Measuring glasses tested at five points .	0	1	9

Instruments which fail to reach the required standard of accuracy are not marked, and half the above fee is charged.

July, 1903.

NOTE ON FILTRATION IN DETERMINATIONS OF CRUDE FIBRE.*

By R. W. THATCHER.

All analysts of food products, or feeding-stuffs, are familiar with the difficulty which is often experienced in filtering off the acid and the alkaline liquids in the determinations of crude fibre by the official method of the Association of Official Agricultural Chemists. Hence I wish to suggest the following modification of the usual procedure, which I have found to give very satisfactory results :—

Select a funnel of sufficient size to contain the entire bulk of the mixture to be filtered, and fit into its point a small platinum filtering cone. Introduce enough ignited asbestos-wool to fill the cone a little more than full. Upon moistening, the wool softens into a fluffy mass, which may be drawn down into a firm, close filter by suction. The mixture to be filtered is now poured into the funnel, with the usual care to avoid disturbing the asbestos layer, and suction is applied. The filtrate obtained in this manner has always been found to be free of suspended particles of fibre. Filtration is very rapid in all cases except when

* Proceedings of the Nineteenth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, D.C.

working with finely ground flour or spices, which tend to clog the filter and impede the flow of the filtrate. In such cases place the funnel in an ordinary jacket of boiling water or steam in order to secure hot filtration, transfer the entire mass to be filtered to the funnel, and apply the suction as usual. Filtration will then proceed at the desired temperature and without further attention from the operator, thus avoiding the two objections to the use of the Gooch filter as recommended in the official method. After filtration and washing are complete, transfer the contents of the funnel to a platinum evaporating dish, rinsing the last particles of fibre from the funnel to the dish with a fine jet of distilled water. Evaporate off the water thus used, dry to constant weight, and complete the determination as usual. I prefer this mode of operation to the use of a paper filter, with correction for loss of weight sustained by the paper in a blank determination, as suggested by Winton ("Conn. Agr. Expt. Sta. Report," 1898, p. 189; and *Bull.* 65, Bur. of Chem., U.S. Dept. Agri., pp. 58, 154, and 155), for the reason that, in addition to the possibility of obtaining additional fibre from the paper used in the acid filtration, I have found that duplicate determinations of the correction to be applied do not always give concordant results, probably because of variations in the weight and composition of individual filters in any given pack of them. I have used the method outlined above for several years and upon a great variety of samples with uniformly satisfactory results. In the cases where filtration is slow it proceeds without attention from the analyst, thereby relieving the tediousness of the operation very materially.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 3, July 20, 1903.

Estimation of Traces of Arsenic.—Armand Gautier.—The new method of estimation of traces of arsenic which the author employs is of extreme simplicity, and can be used to detect minute traces of arsenic in animal organisms. The method is founded on the principle that when arsenic exists, even in very small proportion, in conjunction with iron in a mineral or potable water, the iron, when oxidised or precipitated, retains all this arsenic. The salt used is a polyferric sub-salt, and the extraction of the arsenic is so complete in this case that, under the experimental conditions which the author employs, 1/100oth of a m.grm. of arsenic, added either in the form of arsenite or arsenate to a litre of pure water is entirely removed by the iron and can be absolutely estimated,

Curves of Sublimation.—A. Bouzat.—The author showed, in a previous research, that the curves of dissociation of the group sol. $\rightleftarrows$ sol. + gas are deduced one from the other by a very simple law. The proportion of the absolute temperatures corresponding to the same pressure in any two systems whatsoever of the group remain constant for that pressure. The vaporisation and sublimation can be deduced from the dissociation.

Law of the Re-combination of Ions.—P. Langevin.—When gases are rendered conductors of electricity, they justify in all their properties the hypothesis that the charges are carried by an infinite number of electric centres or ions—some being positive, some negative, all having the same charge in absolute value as that which transports a monovalent atom in electrolysis. The author finds that recombination takes place when, in the relative movements of the particles, the centres of two ions at the moment of perihelion are at a distance from one another less than a constant distance, σ. The author also finds that the coefficient of re-combination, α, is proportional to the pressure.

Catalytic Actions of Metals.—A. Trillat.—The author investigates the catalytic action of copper and platinum with regard to oxidation, dehydrogenation, condensation, and saponification, and finds, in all cases, that the catalytic action of metals is very complex.

Ferrisulphuric Acid and Ethyl Ferrisulphate.—A. Recoura.—The author shows that ferrisulphuric acid behaves as a bibasic acid, analogous to chromosulphuric acid. He prepares ethyl ferrisulphate, and also studies the action of heat on ferrisulphuric acid.

Prussian Blue and Turnbull's Blue. A New Class of Complex Cyanides.—P. Chrétien.—Neither Prussian nor Turnbull's blue are either ferrocyanides or ferricyanides. Soluble Prussian blue has a composition $FeCy_6FeK$ or Fe_2Cy_6K, whilst insoluble Prussian blue, which is prepared in the presence of an excess of a ferric salt, has the composition $Fe_7Cy_{18},13H_2O$. Turnbull's blue has formula $Fe_5Cy_{12},8H_2O$ or $(Fe_2Cy_6)_2Fe,8H_2O$, and is the ferrous salt corresponding to the soluble blue. The author makes a thermometric study of these substances and the cyanide complex which they contain.

Spartein: General Characteristics; Action of certain Reducing Agents.—Ch. Moureu and A. Valeur.—Spartein is a liquid volatile alkaloid which has been employed in therapeutics for the past twenty years, under the form of sulphate, in the treatment of cardiac ailments. The authors investigate the physical constants of this substance, and give certain general indications as to its chemical nature. Its great stability with regard to reducing agents lead to the conclusion that the base is saturated, and that all the liaisons between the atoms are simple ones. After a single investigation of the crude formula, little doubt remains that the molecule contains two, and perhaps three, closed chains.

Isonitrosomalonic Ethers and their Transformation into Mesoxalic Ethers.—L. Bouveault and A. Wahl.—V. Meyer and A. Müller have shown synthetically that nitrosomalonic acid is in reality an isonitroso-derivative identical with the oxime of meso-oxalic acid. It follows from this that the isonitrosomalonic ethers, $NOH=C<^{CO_2R}_{CO_2R}$, constitute the oximes of the corresponding meso-oxalates, $CO<^{CO_2R}_{CO_2R}$. These latter bodies being difficult of preparation, the authors obtain them by saponification of their oximes and investigate their properties.

Action of Ammonia on Ethylene Oxide of β-o-Cyclohexanediol.—Léon Brunel.—In a previous paper the author describes the preparation of certain addition products of ethylene oxide of β-o-cyclohexanediol. He now investigates the compounds obtained by the action of NH_3 on this ether, and obtains the following compounds:—Orthoaminocyclohexanol, $OH{\cdot}C_6H_{10}{-}NH_2$; and, by reducing the proportion of ammonia, obtains two isomeric dioxycyclohexylamines, $OH{-}C_6H_{10}{-}NH{-}C_6H_{10}{-}OH$.

No. 4, July 27, 1903.

Preparation and Properties of Ruthenium Silicide.—Henri Moissan and Wilhem Manchot.—At the temperature of fusion of ruthenium this metal easily combines with silicon to give a silicide of formula RuSi, of density 5·40, perfectly crystalline, of great hardness, and very stable in presence of a large number of reagents.

Arsenic in Sea-water, Table Salt, Mineral Waters, &c.; its Estimation in certain ordinary Reagents.—Armand Gautier.—It has been known for some time that sea-water contains a small proportion of arsenic. The author estimates, by his method described in a recent paper, the arsenic in the water 30 km. from the coast of Brittany under the three forms—mineral, organic, and organised. Similar estimations are made on the arsenic in mineral waters and in the principal reagents used for the detection of this substance in physiology.

A Combination of two Bodies which on raising the Temperature Unite, and which Separate below – 79°.—D. Grenez.—Acetone forms with mercuric iodide a solid orange-yellow combination, which is produced by the elevation of temperature a little above –94·9°, but which is only stable up to the temperature of –79°, at which temperature it is completely destroyed.

Simultaneous Separation and Estimation of Baryta, Strontia, and Lime.—Lucien Robin.—The author describes a simple method for the separation and estimation of the three metals of the alkaline earths simultaneously when present in acid solution. The liquid is first rendered alkaline by ammonia, acidified with acetic acid, boiled, and potassium bichromate added in excess. The baryta is separated as chromate. The strontia is next separated by rendering the filtrate ammoniacal, boiling it, and introducing pure ammonium sulphate. The strontia is weighed as sulphate.

Condensation of Acetylenic Ethers with Alcohol.—Ch. Moureu.—Methyl phenylpropiolate, under the action of sodium methylate, can fix 2 or 1 mols. of methylic alcohol by the total or partial saturation of the acetylenic function. The new compounds thus formed correspond to benzoylacetic and cinnamic acids. The yield is usually about four-fifths of the theoretical yield.

Constitution of Allyl Cyanide.—R. Lespieau.—Allyl cyanide is prepared by the action of potassium cyanide in the cold on allyl bromide, and as a result of the author's researches on this substance he believes it to correspond to the formula $CH_2=CH—CH_2CN$.

Quinone-diketones. — Œchsner de Coninck. — The author's researches lead him to believe that the molecule of the quinone-diketones, quinone-phenols, &c., at a given temperature, and under the influence of H_2SO_4, rupture between the group CO and the substituted or non-substituted benzenic group. Afterwards these latter groups are decomposed and act on sulphuric acid, which is energetically reduced. By this means the rapid and abundant evolution of SO_2, which the author observes in all his experiments, is explained. Alizarine and purpurine are less resisting than anthraquinone.

Albumenoid matter in Maize Seed.—MM. Donard and Labbé.—The authors continue their research on the special properties of maisine, the albumenoid matter extracted from maize by means of boiling amylic alcohol.

MISCELLANEOUS.

Appointment.—Messrs. Howards and Sons inform us that they have entrusted to Mr. Edward White, B.Sc., F.I.C., the management of that branch of their business dealing with the manufacture of fine chemicals, and carried on under the style of Messrs. Hopkin and Williams, at Cross Street, Hatton Garden, E.C., which until recently was under the management of the late H. C. Everson, F.I.C. Messrs. Hopkin and Williams have a newly-built and equipped factory at Ilford, where the laboratories afford ample scope for research work in chemical technology and extension of business under Mr. White's direction. Mr. White, who is a Bachelor of Science of London University, and a Fellow of the Institute of Chemistry, was formerly Bell Scholar in the Pharmaceutical Society's School, acting afterwards as Demonstrator in the chemical laboratories at Bloomsbury Square. For the last fourteen years he has been in charge of the Pharmaceutical Department at St. Thomas's Hospital, where he has carried out original work dealing with pharmaceutical chemistry, one of the latest contributions from his laboratory being the solution of the time-honoured kino gelatinisation problem. Mr. White is also well known as joint-author of "Pharmacopedia," and as the compiler of the last edition of the "St. Thomas's Hospital Pharmacopœia." At the recent Bristol meeting of the British Pharmaceutical Conference he was appointed one of the Honorary General Secretaries to fill the vacancy caused by the retirement of Mr. F. Ransom.

UNIVERSITY COLLEGE, BRISTOL.
CHEMICAL DEPARTMENT.
Professor—SYDNEY YOUNG, D.Sc., F.R.S.
Lecturer—FRANCIS E. FRANCIS, D.Sc., Ph.D.
Demonstrator—OLIVER C. M. DAVIS, B.Sc.
The SESSION 1903-4 begins on October 6th. Lectures on Inorganic, Organic, and Advanced Chemistry will be delivered during the Session. The Laboratories are fitted with the most recent improvements for the study of Practical Chemistry and Metallurgy in all its branches. In the Evening the Laboratory is opened and Lectures on Inorganic Chemistry, at reduced fees, are delivered. Several Scholarships are tenable at the College.
CALENDAR, containing full information, price 1s. (by post, 1s. 4d.).
For Prospectus and further particulars apply to—
JAMES RAFTER, Registrar and Secretary.

THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.
SESSION begins Monday, SEPTEMBER 21st, 1903.
The DIPLOMA of the COLLEGE is granted in the following Departments:—CIVIL, MECHANICAL, ELECTRICAL, CHEMICAL, and MINING ENGINEERING; NAVAL ARCHITECTURE, ARCHITECTURE, METALLURGY, MATHEMATICS and PHYSICS, and CHEMISTRY.
The COURSES of STUDY for the Diploma extend over three Sessions. The average fee per Session is £12 12s. SPECIAL COURSES for individual Students are arranged as required. HOLDERS of the DIPLOMA are eligible for the DEGREE of B.Sc. in ENGINEERING of the UNIVERSITY of GLASGOW after attendance for at least One Session upon prescribed University Classes.
The LABORATORIES in the DEPARTMENTS of PHYSICS, CHEMISTRY, METALLURGY, MECHANICAL, and ELECTRICAL ENGINEERING, are equipped with the most approved apparatus.
The Preliminary Examination for Candidates for the Diploma begins on September 14th. Names of intending Candidates must be lodged not later than September 11th.
The CALENDAR (price, by post, 1s. 4d.) and PROSPECTUS (gratis) will be sent on application to the SECRETARY, 38, Bath Street, Glasgow.

REDRUTH SCHOOL OF MINES, CORNWALL.
Session 1903-1904 begins September 9th.
A "Mining Certificate" is awarded to Students passing successfully through the School Course.
PRACTICAL MINING CLASSES, under the Instruction Capt. W. HAMBLY (late Government Inspector, South Africa).
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UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; one commencing on September 15th, one on the second Monday in January, and the third on the second Monday in June (or July, as may hereafter be determined).

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations (except that in September) may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must apply to the Principal for a Form of Entry, which must be returned within a specified time before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Principal, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination must pay a Fee of £2. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following five subjects:—(1) English; one paper of three hours. (2) Elementary Mathematics; two papers of three hours each. (3) Latin or Elementary Mechanics, or Elementary Physics—Heat, Light, and Sound, or Elementary Chemistry, or Elementary Botany; one paper of three hours in each subject. (4) and (5) Two of the following subjects, neither of which has already been taken under Section (3); one paper of three hours in each subject; if Latin be not taken, one of the other subjects selected must be another Language from the List, either ancient or modern:—Latin, Greek, French, German, *Arabic, *Sanskrit, *Spanish, *Portuguese, *Italian, *Hebrew, Ancient History, Modern History, Logic, Physical and General Geography, Geometrical and Mechanical Drawing, Mathematics (more advanced), Elementary Mechanics, Elementary Chemistry, Elementary Physics—Heat, Light, and Sound, Elementary Physics—Electricity and Magnetism, Elementary Biology—Botany, *Elementary Biology—Zoology. Candidates for Examination in subjects marked with an asterisk must give at least two months' notice; there will be no Examination in them in September, 1903.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

Several valuable Scholarships and Exhibitions are available to students.

Intermediate Examination in Science.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. Examination.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously, and to have passed the Matriculation Examination at least three years previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry two papers will be set and a practical examination.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

Doctor of Science.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with the Form of Entry he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis.

Preliminary Scientific (M.B.) Examination.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, F.R.S.
Lees Reader in Chemistry—A. Vernon Harcourt, F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, J. Watts, V. H. Veley, F.R.S., J. E. Marsh.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.
Jacksonian Professor of Natural and Experimental Philosophy—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Emmanuel, Sidney, Pembroke, Caius, and Downing Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar.*

UNIVERSITY OF DUBLIN.

Trinity College.

Professor of Chemistry—(Vacant).
Assistant Lecturer—Emil A. Werner, F.C.S., F.I.C.
Demonstrator—W. C. Ramsden, F.C.S.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 2nd of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; Advanced, including Physical Chemistry, second year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Freshmen, and tenable for five years. These Foundation Scholars receive £20 per annum, have free commons, their chambers for half the charge paid by other students, and their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(Division of Engineering, Architecture, and Applied Science).

Professor of Chemistry—J. M. Thomson, F.R.S., F.C.S.
Lecturer—Herbert Jackson, F.C.S.
Demonstrators—P. H. Kirkaldy, F.C.S., and D. Northall Laurie, F.C.S.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1903-1904 are October 1, January 13, and April 20.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s.; per ann., £8 8s.; Practical Chemistry per term, £4 4s.; per ann., £10 10s.; Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

METALLURGY.

Professor—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Fee, £3 3s. for the Course.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, F.R.S., F.C.S.

In addition to the regular College Course in Photography occasional classes may be formed. For further particulars application should be made to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professors—Sir William Ramsay, LL.D., F.R.S., &c. (Inorganic and Physical Chemistry); J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry).

Assistants—Morris Travers, D.Sc.; E. C. C. Baly, F.I.C.; N. T. M. Wilsmore, M.Sc.; and S. Smiles, D.Sc.

The Session is divided into three Terms, as follows:—First Term, from October to December; Second Term, from January to March; Third Term, from April to June. Class Examinations begin in June.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 9. Practical, Friday, 2 to 2.30, or 3.30 to 5. Fee, £10 10s.

This Course treats of the chief physical and chemical characters of the Non-metallic Elements, their preparation and characteristic tests.

Junior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fees:—For the Course, £7 7s.; for the First or Second Terms, £4 4s.

In this Course the physical principles bearing on Chemistry, are first discussed, and the Chemistry of the Elements and their compounds are treated in considerable detail, under the headings—Elements; halides, oxides, sulphides, &c., borides, carbides and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 and on Wednesdays at 11, on the chief types of Carbon Compounds.

An Exercise Class will meet once a week throughout the Session.

Senior Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning in January.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

The Principles of Chemistry will be specially considered, comprising the Atomic Theory, Chemical Classification, the Periodic Law, Thermal Chemistry, Dissociation, the Application of Physical Methods to the Solution of Chemical Problems, and the influence of Mass and Temperature on the progress of Reactions. Special attention is paid to the most recent researches bearing on Chemical Theory.

Third Term: Some Lectures will also be given on Saturdays at 9, during the Third Term, on the History of Chemistry.

Organic Chemistry.

Mondays, Wednesdays, and Fridays, at 9, during the session.

This Course will consist of three lectures a week during the whole Session, and is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the preceding Course, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

An Advanced Course will be held twice a week during the First, Secoud, and third Terms, for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor of Chemistry—W. A. Tilden, D.Sc., F.R.S.

Assistant Professor—M. O. Forster, Ph.D., D.Sc.

Demonstrators—H. Chapman Jones; G. T. Morgan, D.Sc., A.R.C.S.; and J. C. Philip, M.A., Ph.D., B.Sc.

Assistants—G. S. Newth and H. Burrows, Ph.D.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Board of Education. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science. The Associateship

of the Royal College of Science is given in one or more of the following divisions :—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction lasts for three years, is the same for all the divisions during the first year, after which it is specialised according to the particular division in which the student is working for the Associateship.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject except Mining and Metallurgy and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
	£	£
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	

The fee for the course of Mine Surveying is £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to £40.

The Session is divided into two Terms. The first Term begins about the first week of October, and ends about the middle of February. The second Term begins in the middle of February, and ends about the middle of June.

The hours of study are from 10 a.m. to 1.15, and from 2 to 4 or 5 p.m. every day, except on Wednesday and Saturday, when the College closes at 1 p.m.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Sixty-second Session will commence on Oct. 1, 1903.

Professors—Chemistry, W. Palmer Wynne, D.Sc., F.R.S., F.I.C. Sec. C.S.; Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S. (Dean).

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Richard Bremridge, Secretary and Registrar, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

University of Wales.

Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Demonstrators—H. Hibbert, M.Sc. (Vic.), and A. Brooke, Ph.D. (Strassburg).

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

Lecturer on Dyeing—E. J. Wilkinson.

The College is open to male and female students above the age of sixteen years. The Session commences on Sept. 28th, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Matriculation Course; two lectures weekly throughout the Session. (2) Intermediate Science Course; four lectures weekly throughout the Session. (3 and 4) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1903-1904, Course B). (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spentat Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 15, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Pros-

pectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A Constituent College of the University of Wales.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D. Demonstrator, Alexander Lauder, B.Sc., F.C.S. Assistant Lecturer in Agricultural Chemistry, Alan Baguley, B.Sc. Scholar Assistant, C. K. Tinkler.

Physics.—Professor, E. Taylor Jones, D.Sc.

The Session opens October 1st, 1903. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrators—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 7th, and terminates on June 26th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of about 80 lectures on Organic Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Lecturer—Francis E. Francis, D.Sc., Ph.D.

Demonstrator—Oliver C. M. Davis, B.Sc.

The session 1903-1904 will begin on October 6. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Registrar and Secretary.

Day Lectures.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Elementary Course.—Two Lectures a week will be given during the Session. Fee, £4 4s.

Special Course.—A special course of Lectures is also given to Engineering Students.

Intermediate Course.—Three Lectures a week will be given throughout the Session. Fee, £5 5s. There will be tutorial classes in connection with the Elementary and Intermediate Courses.

Advanced Course (Parts I. and II.).—One Lecture a week

in each part will be given throughout the Session. Fee for each course, £2 12s. 6d.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given throughout the Session. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session. Fee, £2 12s. 6d.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, Metallurgy, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session	15	12½	10	7½	5
,, Two Terms ..	11	9	7½	5½	3½
,, One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical and a Metallurgical Scholarship each of £25 are offered for competition.

Evening Lectures.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

Pharmaceutics.—During the first and second Terms a course of Lectures will be given one evening a week dealing chiefly with the Materia Medica, Pharmacy, and Chemistry of the British Pharmacopœia. Fee, £1 1s.

Practical Chemistry—Laboratory Instruction.—The Laboratory will be open two evenings a week from 7 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—(Two Terms) Two Evenings, 25s.; One Evening, 15s. (One Term) Two Evenings, 15s.; One Evening, 10s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Registrar and Secretary.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

Chemistry and Metallurgy.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.

Lecturers—G. P. Darnell Smith, B.Sc., F.I.C., F.C.S; H. A. M. Borland, A.R.C.S.; A. J. Carrier, B.Sc.

Demonstrators—E. H. T. Parker; H. C. Shilstone; H. R. Tutton.

Assistant in Chemical Laboratory—C. E. Young.

The Laboratories of this Department are open during the Term on every week-day as a School of Practical Chemistry, Analysis, and Assaying, to Students of either sex. They include the Junior Laboratory (for forty Students working at one time), Senior Laboratory, Gas Analysis Room, Balance Room, Combustion Room, Store Rooms, and Metallurgical Laboratory. Each Student works independently, and receives individual instruction and help.

The training in this Department is intended to fit Students to become Professional Chemists, to prepare them for Medical or Pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture, and to train them in practical Metallurgical processes, especially Assaying.

Special facilities will be given to Students wishing to undertake research work approved by the Principal; and the Courses provide completely for the Preliminary Scientific Examination (M.B.), and for the Examinations in Chemistry for the B.Sc. degree of the University of London.

The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics, is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute, provided the details in each case be certified by the Professors.

Certificates of Proficiency in Assaying will be given to Students who complete a Course of not less than two years' work in the Metallurgical Department, and pass satisfactorily the College examinations in the Theory and Practice of Assaying.

The Laboratories are open every week-day from 9 till 12 noon, and from 1.30 to 4.30 p.m., except Saturday, when they close at noon.

The Annual Fee of £10 10s. secures (in addition to the use of either or both Laboratories) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and the Engineering Workshop.

The College Evening Classes, available to persons of either sex, will commence on Monday, September 28th.

Further detailed information may be obtained from the College Prospectus, price 6d.

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S.

Assistant Lecturers and Demonstrators—Alex. McKenzie, M.A., D.Sc., Ph.D.; Alex. Findlay, M.A., D.Sc., Ph.D.

The Session will be opened on October 5th, 1903.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Four hours weekly during the Winter and Spring terms. Mondays to Thursdays inclusive, at 9.30 to 10.30 a.m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9 30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—Advanced Organic Chemistry.—This course extends over two years, and is divided into two parts:—(*a*) Carbon Compounds of the Fatty Series; (*b*) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *General and Physical Chemistry.*—This course will deal in outline with the more recent developments of Theoretical Chemistry. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General, Physical, and Organic Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Practical Chemistry.

The instruction in Practical Chemistry extends over three years. The Laboratory will be open daily from 9.30 to 5, except on Saturdays, when it will be closed at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of about £96 is awarded annually in September.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

BRADFORD MUNICIPAL TECHNICAL COLLEGE.

Department of Chemistry and Dyeing.

Head of Department—W. M. Gardner.

Lecturers in Chemistry—B. North, A.R.C.Sc. (Lond.); S. F. Stell, F.C.S.; and W. Trotter.

Lecturer in Physics—J. A. Tomkins, A.R.C.Sc. (Lond.).

Lecturer in Dyeing—A. B. Knaggs, F.C.S.

Lecturer in Metallurgy—W. J. Willis.

Lecturer in Gas Manufacture—W. Cranfield.

Lecturer on Botany, Biology, and Pharmacy—W. West, F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided:—

I. *General Chemistry Course*, extending over three years, including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Chemical Philosophy, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over three years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering.* Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science.* One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing.* Extending over one or two years.

VI. *Textile and Dyeing.* Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.), London.*—Attendence at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course.* Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on three half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

IX. Attendance at the College Courses and College Certificates in Chemistry, Physics, Animal Biology, and Botany are recognised by the Conjoint Board for Medical Studies.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

Chemical Department.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY. THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Lecturer in Organic Chemistry—Julius B. Cohen, Ph.D.

Assistant Lecturers and Demonstrators—T. S. Patterson, Ph.D., and H. M. Dawson, B.Sc., Ph.D.

Demonstrators—C. E. Whiteley, M.Sc., and W. Lowson, B.Sc., A.I.C.

The Session begins October, 1903.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. Advanced Inorganic Chemistry.—Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Advanced Inorganic Chemistry.—Non-metals. Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.

5. Honours Courses—

(*a*) Organic Chemistry.—Monday, Wednesday, and Friday at 12 noon in the First and Second Terms. Fee, £2 12s. 6d.

(*b*) History of Chemistry.—Monday, Wednesday, and Friday at 9.30 a.m. in the First Term. Fee, £1 11s. 6d.

(*c*) Physical Chemistry.—Tuesday, Thursday, and Saturday at 9.30 a.m. in the Second and Third Terms. Fee, £2 12s. 6d.

(*d*) Electro-chemistry.—One hour weekly. 31s. 6d.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m.

to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session.—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 p.m., from January to March. Fee, £5 5s.

Elementary Science for Teachers.—Saturdays, 9.30 to 12.30, for half the session. £2 12s. 6d.

Dyeing and Tinctorial Chemistry Department.

Professor—Arthur G. Green, F.I.C.

Lecturer and Research Assistant — A. G. Perkin, F.R.S., F.I.C.

Assistant Lecturer—A. B. Steven, B Sc.

Assistant Lecturer and Demonstrator of Practical Dyeing—Percival J. Wood.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, F.I.C.

Assistant Lecturer and Demonstrator—F. Kopecky.

Demonstrator—Harold Brumwell.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Salt, Akroyd, Brown, Baines, Emsley, Craven, Wheatley, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the Yorkshire College.

UNIVERSITY OF LIVERPOOL.

Professor—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers — A. T. de Mouilpied, B.Sc., Ph.D.; and A. W. Titherley, D.Sc., Ph.D.; F. J. Brislee, B.Sc.

Assistant—H. H. Froysell.

The Session commences October 1st.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool, London, and Edinburgh; for the Pharmaceutical Diplomas; for a special Technological Certificate of the University; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £4.

Pharmacy Courses: Junior, £3; Senior, £3.

Dental Course, Lectures and Practical. Fee, £5 5s.

Course A.—Non-metals. Fee, £3.

Course B.—Metals. Fee, £3.

Course C.—Organic Chemistry. Fee, £3.

Course H.—Special Organic Subjects. Fee, £2.

Course D.—Physical Chemistry, with Practical Work. Fee, £2.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F. — Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metallurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Distillation of Coal and Tar Industries. (6) Fuel and Gas. (7) Chemistry Applied to Sanitation. (8) Technical Gas Analysis. (9) Electrochemical work. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Preliminary. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances; preparation of Inorganic Compounds. (3) Revision Class. (4) Senior: Practical Organic. (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Examination of Water and Air, &c. (6) Quantitative Class.

Chemical Laboratory.

The Chemical Laboratories recently enlarged provide accommodation for every kind of chemical and metallurgical work and research. They include thirty rooms devoted to the study of Chemistry and Metallurgy. Separate rooms are provided for Organic Work, Quantitative Analysis, Water Analysis, Gas Analysis, Photometry and Photography, Electro-chemical Work, Metallurgy Laboratories, and a Research Laboratory. New stores for students' apparatus and chemicals have also been built and placed in charge of a skilled dealer.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, Elementary Engineering, Drawing, and Design (in this or one of the following years). German. Or, the University Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Course C, on Organic Chemistry, Lecture Course D or E, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the B.Sc. Degree of the University of Liverpool, or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—In the third year the student should begin to specialise. The following are possible alternatives:—1. Courses D, E, and F; Course H. Any other Courses omitted in a previous year. Laboratory, five days per week. The Degree of B.Sc. in the Honours School of Chemistry may be taken. 2. Metallurgical Classes. Metallurgical Laboratory, two days per week. Chemical Laboratory, Gas Analysis, and Electro-chemistry, two days per week. Physical and Electrotechnical Laboratory, one day per week. 3. Courses D, E, and F. Physics (Senior Course). Chemical Laboratory, four days per week. Physical Laboratory, one day per week. 4. Courses D and F, and a course on Chemistry applied to manufacturing operations. Chemical Laboratory, three or four days per week. Engineering Laboratory and Electrotechnical Laboratory, one day per week.

Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry may be taken after 1, 2, or 3. Those who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Examination in any subsequent year.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1903, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the College Secretary not later than November 15, 1903. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held during the winter.

The Prospectus containing full particulars may be obtained from the Secretary, University of Liverpool.

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—F. C. Garrett, M.Sc., F.C.S.

Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturers and Demonstrators—J. A. Smythe, M.Sc., Ph.D., and H. W. Cousins, B.Sc.

First Year Courses.—I. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 7th. Fee, £3 10s. for the Session.

II. *Special Course.*—More advanced than the above. Mondays and Fridays, 11 to 12. Fee, £3 10s. for Session.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 6th. The class for Inorganic Chemistry meets at 11 a.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s. Also special class in Crystallography.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m.

Metallurgy and Assaying.—Lecturer, Professor Louis, M.A., F.I.C., F.C.S.; Demonstrator, G. H. Stanley, A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the three following examinations:—

1. The first examination for the Degree of B.Litt.
2. Durham Examination for certificate of proficiency in General Education, held in March and September.
3. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Science.—Every candidate for the Associateship in Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the second year in an examination in a more advanced stage in any two of these subjects. Associates in Science are admissible one year after obtaining the title of Associate to the examination for the degree of Bachelor of Science of the University of Durham.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 28th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing September 28th. Candidates should send in their names to the Secretary on or before September 21st.

OWENS COLLEGE, THE VICTORIA UNIVERSITY OF MANCHESTER.

Professor and Director of the Chemical Laboratory—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers—George H. Bailey, D.Sc., Ph.D.; W. A. Bone, D.Sc.; D. L. Chapman, B.A.; Norman Smith, B.Sc.; F. V. Darbishire, B.A., Ph.D.

Demonstrator in Organic Chemistry—D. T. Jones, B.Sc.

Lecturer in Technical Organic Chemistry—Jocelyn F. Thorpe, Ph.D.

Lecturer in Metallurgy—Dr. Bone.

Lecturer in Electro-Chemistry—R. S. Hutton, B.Sc.

The Session begins on October 6, 1903.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Tuesdays, Thursdays, Saturdays, 11.30 a.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, 9.30, during two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Thursdays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 9.30, during the Session.

Chemical Laboratories.—These are again being extended. Two large rooms will be added to the main laboratories; one for Inorganic and one for Organic work. These will connect the present buildings to the Schunck Laboratory. The Laboratory and Chemical Library belonging to the late Dr. E. Schunck, F.R.S., left by him in 1902 for the use of the Owens College, is being erected erected in Burlington Street. The Schunck Laboratory is to be devoted to research work.

The Chemical Laboratories are open daily from 9.30. a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Metallurgy.—*Lectures*: (A) The Metallurgy of Copper, Lead, Silver, Gold, Zinc, and Antimony; and (B) the Metallurgy of Iron and Steel.

The Metallurgical Laboratory, which is open every day in the week, has recently been re-equipped with a view to research work on the structure and properties of Steel and other Alloys, and the Chemistry of Fuel and Gases.

Electro Chemistry.—In connection with the new John Hopkinson Memorial Laboratory, rooms have been fitted for the study of Electricity in its applications to Chemistry. There is a complete equipment for Electro-chemical and Electro-metallurgical work. Demonstrator and Assistant Lecturer in Electro-technics, Robert Beattie, B.Sc. (Durham). Demonstrator and Assistant Lecturer in Electro-chemistry, R. S. Hutton, M.Sc. (Vict.).

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry or Metallurgy Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £100 is awarded annually among the Graduates in Science for the encouragement of Research. Among the *College* Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; &c.

Schunck Fellowship.—A Fellowship for Chemical Research will be offered during the Session 1903-4 under the Schunck endowment, a portion of the income arising from which is at present used for providing expensive material required in research work. Students may be appointed to Research Studentships, which entitle the holders to work in the laboratories under reduced fees.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—Natural and Artificial Dye-stuffs, and the Principles of Dyeing and Printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

For further particulars apply to the Registrar, Mr. S. Chaffers.

UNIVERSITY COLLEGE, NOTTINGHAM.

Departments of Chemistry and Metallurgy.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; G. D. Lander, D.Sc.; and G. Sand, Ph.D., M.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 5th, for both Day and Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on Electrochemistry and other special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations. Special lectures will also be given in Pharmacy, Materia Medica, and all other Pharmaceutical subjects.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

UNIVERSITY COLLEGE, SHEFFIELD.

Professor of Chemistry—W. Carleton Williams, B.Sc., F.C.S.

Lecturer—G. Young, Ph.D., F.R.S.E.

The Session will commence on October 1st.

Matriculation Course.—Tuesday and Friday 10 to 11. Fee, £2 12s. 6d.

Intermediate Course.—Inorganic Chemistry. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Organic Chemistry.—Elementary: Saturdays, 10 to 11; fee, £1 1s. Honours: Tuesdays and Thursdays, 12 to 1; fee, £2 12s. 6d. Advanced: Thursdays, 4 to 5; fee, £1 11s. 6d. Special Course: Hours to be arranged; £1 1s.

Physical Chemistry.—Tuesday, 11 to 12. Fee, £1 11s. 6d.

Chemical Philosophy.—Thursday, 11 to 12. Fee, £1 11s. 6d.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health and for the Licentiate of Sanitary Science, willl be held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9. Sessional Fee, Lecture Class and Laboratory, on Wednesday evening, £1 10s. Fee for one term, 17s. 6d.

Department of Metallurgy.

Professor of Metallurgy—J. O. Arnold. This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a new laboratory for the study of the micrographic analysis of metals has been completed and fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students engaged in Collieries or Gas-Works.

A new steel works is now being erected in connection with the Sheffield College at a cost of about £10,000. The works are designed to include a two ton open-hearth furnace, a one ton Bessemer plant, and a four-hole crucible melting plant. The works will also be provided with a hammer and rolling mill capable of dealing with four-inch ingots Differential annealing furnaces, oil-brightening and lead-tempering tanks will constitute part

of the new plant. Additional laboratory accommodation will be attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

UNIVERSITY COLLEGE, DUNDEE.

University of St. Andrews.

Professor of Chemistry—James Walker, Ph.D., D.Sc., F.R.S.

Assistant Lecturers—J. S. Lumsden, Ph.D., D.Sc., and J. K. Wood, D.Sc.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins on October 7th, and ends on March 6th. The Summer Session extends from the middle of April to the end of June.

The Junior Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

Chemistry.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Demonstrators—A. N. Meldrum, B.Sc., and F. W. Gray, M.A., B.Sc.

I. *General Lecture Course* (100 *Lectures*),—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Senior Demonstrator, is held in connection with this course.

II. *Special Lecture Course on Organic Chemistry* (50 *Lectures*).—Daily during the Summer Session. Fee, £3 3s.

III. *Practical Course for Medical Students.*—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £4 4s.

IV. *Chemical Laboratory.*—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. Fee, £4 4s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

V. *Physical and Advanced Inorganic Chemistry* (30 *Lectures.*—In connection with the Laboratory work, three Lectures a week on Physical Chemistry and selected portions of Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Mr. A. N. Meldrum. Fee, £2 2s.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

This course is given during the Winter Session, and includes both Lectures and Laboratory work. The Lectures deal with the chemistry of the atmosphere, the soil, manures, and foods. The physiological chemistry of plants and animals, the composition and manurial requirements of crops, and dairy chemistry, are also treated of. The Laboratory work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of soils, manures, feeding stuffs and waters, and with the impurities and adulterations of these, occupy much of the time given to practical work. The fee for the whole course—lectures and practical work—is £3 3s.

UNIVERSITY OF EDINBURGH.

Department of Chemistry.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D.; H. Marshall, D.Sc.; and W. W. Taylor, M.A., D.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to middle of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. An Intermediate Course of Organic and Advanced Inorganic Chemistry is held in summer; fee, £2 2s. There is also a class on History of Chemistry or Chemical Theory, by Dr. Dobbin; fee £1 1s.: and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s.; Oct.-Dec., Jan.-March, or Summer Session, £5 5s. Half Day—Winter Session, £6 6s.; Oct.-Dec., Jan.-March, or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry, including Gas Analysis, Metallurgy, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy, including Anthropology, Physiology, Geology, including Mineralogy, Zoology, including Comparative Anatomy, and Botany, including Vegetable Phy-

siology. In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Chemical Crystallography; History of Chemistry. In the written papers a choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the following subjects, selected by himself:—Gas Analysis; Assaying; Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—Archibald Boon, B.A., B.Sc.; Andrew F. King, F.I.C.; and J. P. Longstaff, B.Sc.

The Session begins September 28th, 1903.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the third year. Special attention will be paid to Electrochemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

Matriculation Fee, 5s.; Composition Fee for Engineering Courses, £12 12s.; for Chemistry Courses, £12 12s., £15 15s. Full particulars are published in the Calendar of the College early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.

Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1903-1904 may be had from Mr. H. F. Stockdale, the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

United College of St. Leonard and St. Salvator.

Professor of Chemistry — T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 13th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for fifty-one Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 25th and following days. Thirty-three of these Bursaries are restricted to Men, four to Men or Women, and fourteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Examinations, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Second B.Sc. Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Examinations in Arts, Science, and Medicine.

The fee for each course of Practical Chemistry is £3 3s.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., F.R.S.E., &c.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The new Chemical Laboratories are now open, and are provided with all modern appliances. Special facilities are offered to those engaged in Research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable for three consecutive years. Also a Junior Fellowship, tenable for four consecutive years, of the annual value of £200.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—Robert Elliott Doran, F.C.S.

The College Session will commence on October 20th, 1903, and end on June 11th, 1904. All classes are open to male and female students.

The courses in Chemistry, though designed primarily to meet the requirements of candidates proceeding to the Examinations in Arts, Medicine, and Engineering of the Royal University of Ireland, of the Medical Licensing Bodies of Dublin and Edinburgh, and of the Pharmaceutical Society of Ireland, can be specially arranged as required, so as to render them suitable to any particular course of study. The following courses are provided:—

Systematic Chemistry.

I. General Lecture Course; three terms. Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.

II. Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.

III. Winter Course of Practical Analytical Chemistry; commencing early in January, 1903.

IV. Summer Course of three months' duration, for students of Medicine; ending about the third week in June.

V. Course for Pharmaceutical Students; held during the second and third terms.

Laboratory Work.

VI. The Chemical Laboratory is open daily from 10 to 4 o'clock, to Students entering for Special Courses of practical work in General Inorganic Chemistry, Qualitative and Quantitative Analysis, Organic Chemistry, or for the purpose of Original Investigation.

Scholarships, &c.—In addition to the Class Prizes given at the Sessional Examinations, the College awards a Senior Scholarship of the value of £40, for Chemistry and Physics (either of which may be taken as a limited course), and numerous Junior Scholarships in Arts, Medicine, and Engineering, of which chemistry forms a part, value from £20 to £24 each, annually. The Royal University of Ireland also offers Exhibitions in Chemistry and Physics, First-class value £42, and Second-class value £21, together with other prizes, *e.g.*, a Studentship of £100 per annum, tenable for three years; and the 1851 Exhibition Scholarships, value £150, tenable for two, and, under certain circumstances, for three years, have from time to time also been placed at the disposal of the College.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c,, are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senier, Ph.D., M.D., F.I.C., F.C.S.

Demonstrator—Thomas Walsh, B.A.

Research Assistants—W. Sloan Mills, M.A., and Francis M. G. Micklethwait, A.R.C.S.

The College Session commences in October and ends in June.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts. — 1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.* — First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts. — 1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.* — 1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.* —1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer a Scholarship of £150 per annum. This Scholarship has just been awarded for the third time to a Chemistry Student of this College, and to another Student it has been renewed for a third year.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Professor of Chemistry—W. N. Hartley, F.R.S.

Lecturer on Organic Chemistry—F. G. Donnan, M.A., Ph.D.

Assistant Chemist—J. Holms Pollok, B.Sc.

Demonstrator of Chemistry and Assaying — A. E. B. Manders.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering

and Manufactures, Physics, and Natural Science. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Organic Chemistry; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students :—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months £12 for the entire session.

The following are supplementary courses of instruction :—

(1) Laboratory Instruction in the Theory of Chemistry. (2) An Analytical Course for Students in Engineering. (3) A Course of Practical Chemistry for Medical Students. (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health. (5) A Course of Chemistry for Pharmaceutical Students.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships include free education for the full Associateseip Course of three years and maintenance allowance of a guinea a week during the Session.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 10d., net. — *City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations begin on Tuesday, September 22nd, and the Winter Session opens on Tuesday, October 6th. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College on Tuesday, September 22nd. Session begins October 6th. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

CITY OF LONDON COLLEGE, White Street, Moorfields. —Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, conducted by Mr. I. S. Scarf, F.I.C., F.C.S., assisted by Messrs. H. W. Harrie, F.C.S., and C. A. West, B.Sc., &c. Session commences Sept. 28.

BATTERSEA POLYTECHNIC.—Principal, Mr. Sidney H. Wells, Wh.Sc. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), assisted by John L. White, M Sc., H. G. Wayling, B.Sc., Mr. H. Evans, Mr. A. Rowan, and others. Session opens Sept. 21. Complete courses of Instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, German, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in Paper Testing, Paper Making, Gas Manufacture, Gas Analysis, Oils, Fats, and Soaps, Chemistry of Building Materials, Chemistry of Foods, &c.

BIRKBECK COLLEGE, Breams Buildings, Chancery Lane. —Chemistry Courses conducted by Dr. J. E. Mackenzie prepares for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmacutical Examinations, Board of Education, &c. This Institution, which has now completed eighty years of educational work in the metropolis, commences its new Session on Monday, September 28th, when an opening address will be delivered by Dr. Emil Reich. The Day and Evening courses of study, comprise the various branches of Natural Science, Mathematics, Classical and modern Languages, Economics, Commercial Subjects, Law, Mental Science, Music, and Art. The courses provide for the Examinations of the University of London, in the faculties of Arts, Science, and Commerce, and also for those of the Conjoint Board, Civil Service, &c. The Report for the last session shows that during the year 67 students passed some university examination, while large numbers gained successes at other public examinations. The College has had many additions to its appliances in recent years, and the Physical, Chemical, Biological, and Metallurgical laboratories are very thoroughly equipped. The Day classes provide courses in Chemistry, Biology, Botany, Physics, Mathematics, and Geology for the Science Degrees of London University, and a complete course of instruction in Metallurgy and Mining. There are also Day classes in Latin, Greek, and modern Languages, including Russian and Spanish. The School of Art is open both day and evening. The Metallurgical laboratory has been extended and reorganised, and classes are held both in the day and evening. The Calendar supplies complete syllabuses of the classes

and full information about the College. A Lecture or Entertainment is given in the Theatre every Wednesday evening.

Brixton School of Chemistry and Pharmacy, 171, Brixton Road, London.—Principal, Dr. A. B. Griffiths, F.R.S.(Ed.). Lectures on Inorganic and Organic Chemistry, Physics, Botany, &c., for Pharmaceutical, Medical, and other students. The benches in the laboratory are fitted with every convenience. There are courses in Research Work. Full particulars as to fees, &c., may be obtained by writing to the Principal.

Borough Polytechnic Institute, 103, Borough Road (near the Obelisk).—Chemistry: Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry (Session fees, per course, 10s. to 20s.). Day Practical class in Electro-chemistry, lecture on Friday evenings (70s.) Special Saturday Morning Class in Practical Chemistry (10s.); Dr. F. Mollwo Perkin, assisted by A. Fontana, B A. Electricity and Magnetism: Evening Lectures and Laboratory Work (Session fees, per course, 10s.), Dr. J. Henderson, assisted by H. Saunders. Special Evening Courses on Painter's Oils, Colours, and Varnishes. Session opens Monday, September 28, 1903.

South Western Polytechnic, Chelsea, S.W.—Principal, Herbert Tomlinson, B.A., F.R.S. Head of the Chemical Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, &c. Systematic Courses are held for the Matriculation, Intermediate Science, and B.Sc. Examinations of the University of London. Prospectuses of Day and Evening Classes may be obtained from the Secretary, 1d. each, by post 3½d.

The Goldsmiths' Institute, New Cross, S.E.—Head of the Chemistry Department, Arthur Lapworth, D.Sc.(Lond.), F.I.C.; Assistants, Mr. A. C. O. Hann and others. Lectures and Practical Classes in General Chemistry and Photography, also in Chemistry applied to other industries, are held in the evenings from 7.15 to 10, and are open to both sexes. Special attention is paid to Technical Laboratory work and the investigation of manufacturing difficulties. Session commences September 21.

East London Technical College, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Assistants, F. G. Pope and Clarence Smith, D.Sc. Lectures and Practical Classes are conducted in the Day Technical College, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., that of the next two years with the degree examination (B Sc). Evening Classes for London University Degrees are also held. The Day College opens on Sept. 21. Evening Classes begin Sept. 28.

University Tutorial College, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

Northampton Institute (City Polytechnic), St. John Street Road, E.C.—Principal, R. Mullineux Walmsley, D.Sc., &c. Lecturers in Technical Chemistry: Mr. S Field, A.R C.S., and Mr. G. Naylor. Day and Evening Classes in Electro-chemistry, Electro-plating, Electro-metallurgy, Electrotyping and Stereotyping. (For full details see Prospectus).

Imperial College of Chemistry and Pharmacy, 49 and 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc. An especial course of instruction is given at this College in Pharmacology and Therapeutics, *re* the Institute of Chemistry Examination. Students attending the College visit technical works.

Carpenters' Company Technical Institute, Jupp Road, Stratford, E.—Principal, William Ping. F.C.S. Evening Classes in Theoretical and Practical Chemistry, and in many other Departments of Science and Art. Day Technical School. Session begins September 21.

Sir John Cass Technical Institute, Jewry Street, Aldgate.—Principal, Charles A. Kohn, M.Sc., Ph.D., &c., assisted by G. Senter, B Sc., Guy D. Ricketts, B.A., and R. S. Willows, D.Sc. Evening Classes in Chemistry, Metallurgy, Physics, and Mathematics, designed to meet the requirements of those engaged in Chemical, Metallurgical, and Electrical industries, and also in other departments of Science and Art. Practical laboratory work. Classes begin September 28. Full details may be obtained on application, or by letter to the Principal.

The Institute of Chemistry of Great Britain and Ireland.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, (i.) to promote the better education of persons desirous of becoming public and technical analysts and chemical advisers on scientific subjects; (ii.) to examine Candidates, and to grant certificates of competency; and (iii.) to elevate the profession of Consulting and Analytical Chemistry by setting up a high standard of scientific and practical proficiency and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship.*—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University approved by the Council, or in the laboratory of a Fellow of the Institute, with the object of adopting the profession of Analytical and Consulting Chemistry. *The Intermediate Examination.*—Candidates for admission to the Intermediate Examination are required to produce evidence (I) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Advanced Mathematics; (ii.) Mechanics and Chemical Engineering; (iii.) Metallurgy; (iv) Geology and Mineralogy; (v.) Physiology; (vi.) Bacteriology; and (III) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' training in a recognised Institution as indicated above, and work systematically for two other years in the laboratory of a Fellow of the Institute. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also passed in at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. *The Final Examination for the Associateship* (*A.I.C.*).—Any Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *Fellowship* (*F.I.C.*).—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of Applied Chemistry in a manner satisfactory to the Council. Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which

may be obtained on application to Messrs. Blundell, Taylor, and Co., 173, Upper Thames Street, London, E.C. Price One Shilling.

Blackburn Municipal Technical School.—Chemistry: Mr. Robert H. Pickard, D Sc.(Lond.)., &c., assisted by Mr. Jos. Yates and Mr. Allen Neville, B.Sc. (Lond.), F.I.C. Session opens Monday, September 14. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 2½d).

Redruth School of Mines, Cornwall.—Principal, J. Paul de Castro, M.A. (Cantab.), A.I C., F.C.S., assisted by a staff of Mining Engineers and Mine Surveyors. Courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Asaying, Mineralogy, and Blowpipe Analysis, for intending Assayers and Mineral Chemists. Shorter Courses are also held in the above subjects to meet the requirements of intending Mining Engineers, and Prospectors. Practical instruction in Mining given at Pednandrea, the School Mine. Syllabus on application to the Registrar. Session commences Wednesday, September 9.

The Municipal School of Technology, Sackville Street, Manchester.—This fine building occupies an area of upwards of 6800 square yards, and is six floors in height. Its equipment, which is nearly complete, is on a scale of great magnitude. It comprises laboratories and workshops for Mechanical, Electrical, and Hydraulic Engineering, for the Textile industries, for Photography, Collotype and Photo mechanical processes, for the Letterpress and Lithographic industries, and for the industries included within the scope of Architecture. The provision for the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises, in addition to ample accommodation for pure Chemistry, laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity.

Leeds Technical School (in connection with the Leeds Institute of Science, Art, and Literature), Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in 41 subjects of Science and Technology, among which are:—Chemistry, Inorganic and Organic, Theoretical and Practical, by Mr. R. E. Barnett, B.Sc., A.R.C.S., Mr. J. B. Murray, and Mr. T. R. White, B.A.; Metallurgy, Theoretical and Practical, and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Magnetism and Electricity, and Practical Physics, by Mr. J. E. Tindall, B.A., B.Sc.; Botany, Lectures and Practical Work, by Mr. N. Walker; Photography, by Mr. S. E. Bottomley. Fees:—Lectures, from 2s. 6d. per Session; Laboratory work, from 2s. 6d. Systematic courses arranged for Pharmaceutical Students and for those engaged in Chemical Industries at composition fees. Session commences Sept. 21st. Prospectuses of various Classes free on application to the Secretary, Mr. Arthur Tait. Calendar of the Institute (196 pp.) post free 5d.

Wolverhampton Municipal Science and Technical School.—Inorganic and Organic Chemistry, Mr. W. Whitehouse, F.C.S.; Physics, Messrs. W. Whitehouse, W. Rogers, and H. J. Tench; Botany, Mr. Sidney Phillips, Ph.C.; Latin, Mr. A. E. Thoseby, B.A., L.C.P. Day Classes in Chemistry and Physics, and Evening Classes in Chemistry, Physics, Botany, French, Latin, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students. Session commences Monday, Sept. 21st. For other particulars and programme, apply Mr. G. F. Chell, Secretary.

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Southport, 1903.

INAUGURAL ADDRESS OF THE PRESIDENT,

Sir Norman Lockyer, K.C.B., LL.D., F.R.S.,
Correspondant de l'Institut de France.

The Influence of Brain-power on History.

My first duty to-night is a sad one. I have to refer to a great loss which this nation and this Association have sustained. By the death of the great Englishman and great statesman who has just passed away we members of the British Association are deprived of one of the most illustrious of our Past-Presidents. We have to mourn the loss of an enthusiastic student of science. We recognise that as Prime Minister he was mindful of the interests of science, and that to him we owe a more general recognition on the part of the State of the value to the nation of the work of scientific men. On all these grounds you will join in the expression of respectful sympathy with Lord Salisbury's family in their great personal loss which your Council has embodied this morning in a resolution of condolence.

Last year, when this friend of science ceased to be Prime Minister, he was succeeded by another statesmen who also has given many proofs of his devotion to philosophical studies, and has shown in many utterances that he has a clear understanding of the real place of science in modern civilisation. We, then, have good grounds for hoping that the improvement in the position of science in this country which we owe to the one will also be the care of his successor, who has honoured the Association by accepting the unanimous nomination of your Council to be your President next year, an acceptance which adds a new lustre to this Chair.

On this we may congratulate ourselves all the more because I think, although it is not generally recognised, that the century into which we have now well entered may be more momentous than any which has preceded it, and that the present history of the world is being so largely moulded by the influence of brain-power, which in these modern days has to do with natural as well as human forces and laws, that statesmen and politicians will have in the future to pay more regard to education and science as empire-builders and empire-guarders than they have paid in the past.

The nineteenth century will ever be known as the one in which the influences of science were first fully realised in civilised communities; the scientific progress was so gigantic that it seems rash to predict that any of its successors can be more important in the life of any nation.

Disraeli, in 1873, referring to the progress up to that year, spoke as follows:—"How much has happened in these fifty years—a period more remarkable than any, I will venture to say, in the annals of mankind. I am not thinking of the rise and fall of Empires, the change of dynasties, the establishment of Governments. I am thinking of those revolutions of science which have had much more effect than any political causes, which have changed the position and prospects of mankind more than all the conquests and all the codes and all the legislators that ever lived" (*Nature*, November 27, 1873, vol. ix., p. 71).

The progress of science, indeed, brings in many considerations which are momentous in relation to the life of any limited community—any one nation. One of these considerations to which attention is now being greatly drawn is that a relative decline in national wealth derived from industries must follow a relative neglect of scientific education.

It was the late Prince Consort who first emphasised this when he came here fresh from the University of Bonn. Hence the "Prince Consort's Committee," which led to the foundation of the College of Chemistry, and afterwards of the Science and Art Department. From that time to this the warnings of our men of science have become louder and more urgent in each succeeding year. But this is not all; the commercial output of one country in one century as compared with another is not alone in question; the acquirement of the scientific spirit and a knowledge and utilisation of the forces of Nature are very much further reaching in their effects on the progress and decline of nations than is generally imagined.

Britain in the middle of the last century was certainly the country which gained most by the advent of science, for she was then in full possession of those material gifts of Nature, coal and iron, the combined winning and utilisation of which, in the production of machinery and in other ways, soon made her the richest country in the world, the seat and throne of invention and manufacture, as Mr. Carnegie has called her. Being the great producers and exporters of all kinds of manufactured goods, we became eventually, with our iron ships, the great carriers, and hence the supremacy of our mercantile marine and our present command of the sea.

The most fundamental change wrought by the early applications of science was in relation to producing and carrying power. With the winning of mineral wealth and the production of machinery in other countries, and cheap and rapid transit between nations, our superiority as depending upon our first use of vast material resources was reduced. Science, which is above all things cosmopolitan—planetary, not national—internationalises such resources at once. In every market of the world

> "things of beauty, things of use,
> Which one fair planet can produce,
> Brought from under every star,"

were soon to be found.

Hence the first great effect of the general progress of science was relatively to diminish the initial supremacy of Britain due to the first use of *material* resources, which indeed was the real source of our national wealth and place among the nations.

The unfortunate thing was that, while the foundations of our superiority depending upon our *material resources* were being thus sapped by a cause *which was beyond our control*, our statesmen and our Universities were blind leaders of the blind, and our other asset, our mental resources, which was within our control, was culpably neglected.

So little did the bulk of our statesmen know of the part science was playing in the modern world and of the real basis of the nation's activities that they imagined political and fiscal problems to be the only matters of importance. Nor, indeed, are we very much better off to-day. In the important discussions recently raised by Mr. Chamberlain next to nothing has been said of the effect of the progress of science on prices. The whole course of the modern world is attributed to the presence or absence of taxes on certain commodities in certain countries. The fact that the great fall in the price of food-stuffs in England did not come till some thirty or forty years after the removal of the corn duty between 1847 and 1849 gives them no pause; for them new inventions, railways, and steamships are negligible quantities; the vast increase in the world's wealth, in Free Trade and Protected countries alike, comes merely, according to them, in response to some *political* shibboleth.

We now know, from what has occurred in other States, that if our Ministers had been more wise and our Universities more numerous and efficient our *mental resources* would have been developed by improvements in educational

method, by the introduction of science into schools, and, more important than all the rest, by the teaching of science by experiment, observation, and research, and not from books. It is because this was not done that we have fallen behind other nations in properly applying science to industry, so that our applications of science to industry are relatively less important than they were. But this is by no means all; we have lacked the strengthening of the national life produced by fostering the scientific spirit among all classes and along all lines of the nation's activity; many of the responsible authorities know little and care less about science; we have not learned that it is the duty of a State to organise its forces as carefully for peace as for war; that Universities and other teaching centres are as important as battleships or big battalions; are, in fact, essential parts of a modern State's machinery, and, as such, to be equally aided and as efficiently organised to secure its future well-being.

Now the objects of the British Association as laid down by its founders seventy-two years ago are "To give a stronger impulse and a more systematic direction to scientific inquiry—to promote the intercourse of those who cultivate science in different parts of the British Empire with one another, and with foreign philosophers—to obtain a more general attention to the objects of science and a removal of any disadvantages of a public kind which impede its progress."

In the main, my predecessors in this Chair, to which you have done me the honour to call me, have dealt, and with great benefit to science, with the objects first named.

But at a critical time like the present I find it imperative to depart from the course so generally followed by my predecessors and to deal with the last object named, for unless by some means or other we "obtain a more general attention to the objects of science, and a removal of any disadvantages of a public kind which impede its progress," we shall suffer in competition with other communities in which science is more generally utilised for the purposes of the national life.

The Struggle for Existence in Modern Communities.

Some years ago, in discussing the relations of scientific instruction to our industries, Huxley pointed out that we were in presence of a new "struggle for existence," a struggle which, once commenced, must go on until only the fittest survives.

It is a struggle between organised species—nations—not between individuals or any class of individuals. It is, moreover, a struggle in which science and brains take the place of swords and sinews, on which depended the result of those conflicts which, up to the present, have determined the history and fate of nations. The school, the University, the laboratory, and the workshop are the battlefields of this new warfare.

But it is evident that if this, or anything like it, be true, our industries cannot be involved alone; the scientific spirit, brain-power, must not be limited to the workshop, if other nations utilise it in all branches of their administration and executive.

It is a question of an important change of front. It is a question of finding a new basis of stability for the Empire in face of new conditions. I am certain that those familiar with the present state of things will acknowledge that the Prince of Wales's call, "Wake up," applies quite as much to the members of the Government as it does to the leaders of industry.

What is wanted is a complete organisation of the resources of the nation, so as to enable it best to face all the new problems which the progress of science, combined with the ebb and flow of population and other factors in international competition, are ever bringing before us. Every Minister, every public department, is involved; and this being so, it is the duty of the whole nation—King, Lords, and Commons—to do what is necessary to place our scientific institutions on a proper footing in order to enable us to "face the music," whatever the future may bring. The idea that science is useful only to our industries comes from want of thought. If anyone is under the impression that Britain is only suffering at present from the want of the scientific spirit among our industrial classes, and that those employed in the State service possess adequate brain-power and grip of the conditions of the modern world into which science so largely enters, let him read the Report of the Royal Commission on the War in South Africa. There he will see how the whole "system" employed was, in Sir Henry Brackenbury's words applied to a part of it, "*unsuited to the requirements of an army which is maintained to enable us to make war.*" Let him read also in the Address of the President of the Society of Chemical Industry what drastic steps had to be taken by Chambers of Commerce and "a quarter of a million of working-men" to get the Patent Law Amendment Act into proper shape in spite of all the advisers and officials of the Board of Trade. Very few people realise the immense number of scientific problems the solution of which is required for the State service. The nation itself is a gigantic workshop; and the more our rulers and legislators, administrators, and executive officers possess the scientific spirit, the more the rule-of-thumb is replaced in the State service by scientific methods, the more able shall we be, thus armed at all points, to compete successfully with other countries along all lines of national as well as of commercial activity.

It is obvious that the power of a nation for war, in men and arms and ships, is one thing; its power in the peace struggles to which I have referred is another. In the latter the source and standard of national efficiency are entirely changed. To meet war conditions, there must be equality or superiority in battleships and army corps. To meet the new peace conditions, there must be equality or superiority in Universities, scientific organisation, and everything which conduces to greater brain-power.

Our Industries are suffering in the present International Competition.

The present condition of the nation, so far as its industries are concerned, is as well known, not only to the Prime Minister, but to other political leaders in and out of the Cabinet, as it is to you and to me. Let me refer to two speeches delivered by Lord Rosebery and Mr. Chamberlain on two successive days in January, 1901.

Lord Rosebery spoke as follows:—

". . . The war I regard with apprehension is the war of trade which is unmistakably upon us. . . . When I look round me I cannot blind my eyes to the fact that, so far as we can predict anything of the twentieth century on which we have now entered, it is that it will be one of acutest international conflict in point of trade. We were the first nation of the modern world to discover that trade was an absolute necessity. For that we were nicknamed a nation of shopkeepers; but now every nation wishes to be a nation of shopkeepers too, and I am bound to say that when we look at the character of some of these nations, and when we look at the intelligence of their preparations, we may well feel that it behoves us not to fear, but to gird up our loins in preparation for what is before us."

Mr. Chamberlain's views were stated in the following words:—

"I do not think it is necessary for me to say anything as to the urgency and necessity of scientific training. . . . It is not too much to say that the existence of this country, as the great commercial nation, depends upon it. . . . It depends very much upon what we are doing now, at the beginning of the twentieth century, whether at its end we shall continue to maintain our supremacy or even equality with our great commercial and manufacturing rivals."

All this refers to our industries. We are suffering because trade no longer follows the flag as in the old days, but because trade follows the brains, and our manufacturers

are too apt to be careless in securing them. In one chemical establishment in Germany 400 doctors of science, the best the Universities there can turn out, have been employed at different times in late years. In the United States the most successful students in the higher teaching centres are snapped up the moment they have finished their course of training, and put into charge of large concerns, so that the idea has got abroad that youth is the password of success in American industry. It has been forgotten that the latest product of the highest scientific education must necessarily be young, and that it is the training and not the age which determines his employment. In Britain, on the other hand, apprentices who can pay high premiums are too often preferred to those who are well educated, and the old rule-of-thumb processes are preferred to new developments—a conservatism too often depending upon the master's own want of knowledge.

I should not be doing my duty if I did not point out that the defeat of our industries one after another, concerning which both Lord Rosebery and Mr. Chamberlain express their anxiety, is by no means the only thing we have to consider. The matter is not one which concerns our industrial classes only, for knowledge must be pursued for its own sake ; and since the full life of a nation with a constantly increasing complexity, not only of industrial, but of high national aims, depends upon the universal presence of the scientific spirit—in other words, brain-power—our whole national life is involved.

The Necessity for a Body dealing with the Organisation of Science.

The present awakening in relation to the nation's real needs is largely due to the warnings of men of science. But Mr. Balfour's terrible Manchester picture of our present educational condition* shows that the warning, which has been going on now for more than fifty years, has not been forcible enough ; but if my contention that other reorganisations besides that of our education are needed is well founded, and if men of science are to act the part of good citizens in taking their share in endeavouring to bring about a better state of things, the question arises : Has the neglect of their warnings so far been due to the way in which these have been given ?

Lord Rosebery, in the address to a Chamber of Commerce from which I have already quoted, expressed his opinion that such bodies do not exercise so much influence as might be expected of them. But if commercial men do not use all the power their organisation provides, do they not by having built up such an organisation put us students of science to shame, who are still the most disorganised members of the community ?

Here, in my opinion, we have the real reason why the scientific needs of the nation fail to command the attention either of the public or of successive Governments. At present, appeals on this or on that behalf are the appeals of individuals ; science has no collective voice on the larger national questions ; there is no organised body which formulates her demands.

During many years it has been part of my duty to consider such matters, and I have been driven to the conclusion that our great crying need is to bring about an organisation of men of science and all interested in science similar to those which prove so effective in other branches of human activity. For the last few years I have dreamt of a Chamber, Guild, League, call it what you will, with a wide and large membership, which should give us what, in my opinion, is so urgently needed. Quite recently I sketched out such an organisation, but what was my astonishment to find that I had been forestalled, and by the founders of the British Association !

* "The existing educational system of this country is chaotic, is ineffectual, is utterly behind the age, makes us the laughing-stock of every advanced nation in Europe and America, puts us behind, not only our American cousins, but the German and the Frenchman and the Italian."—*Times*, October 15, 1902.

The British Association such a Body.

At the commencement of this Address, I pointed out that one of the objects of the Association, as stated by its founders, was "to obtain a more general attention to the objects of science and a removal of any disadvantages of a public kind which impede its progress."

Everyone connected with the British Association from its beginning may be congratulated upon the magnificent way in which the other objects of the Association have been carried out ; but as one familiar with the Association for the last forty years, I cannot but think that the object to which I have specially referred has been too much overshadowed by the work done in connection with the others.

A careful study of the early history of the Association leads me to the belief that the function I am now dwelling on was strongly in the minds of the founders ; but be this as it may, let me point out how admirably the organisation is framed to enable men of science to influence public opinion, and so to bring pressure to bear upon Governments which follow public opinion. (1) Unlike all the other chief metropolitan societies, its outlook is not limited to any branch or branches of science. (2) We have a wide and numerous fellowship, including both the leaders and the lovers of science, in which all branches of science are and always have been included with the utmost catholicity —a condition which renders strong committees possible on any subject. (3) An annual meeting at a time when people can pay attention to the deliberations, and when the newspapers can print reports. (4) The possibility of beating up recruits, and establishing local committees in different localities, even in the King's dominions beyond the seas, since the place of meeting changes from year to year, and is not limited to these islands.

We not only, then, have a scientific Parliament competent to deal with all matters, including those of national importance, relating to science, but machinery for influencing all new councils and committees dealing with local matters, the functions of which are daily becoming more important.

The machinery might consist of our corresponding societies. We already have affiliated to us seventy societies with a membership of 25,000. Were this number increased so as to include every scientific society in the Empire, metropolitan and provincial, we might eventually hope for a membership of half a million.

I am glad to know that the Council is fully alive to the importance of giving a greater impetus to the work of the corresponding societies. During this year a committee was appointed to deal with the question : and later still, after this committee had reported, a conference was held between this committee and the corresponding societies committee to consider the suggestions made, some of which will be gathered from the following extract :—

"In view of the increasing importance of science to the nation at large, your committee desire to call the attention of the Council to the fact that in the corresponding societies the British Association has gathered in the various centres represented by these societies practically all the scientific activity of the provinces. The number of members and associates at present on the list of the corresponding societies approaches 25,000, and no organisation is in existence anywhere in the country better adapted than the British Association for stimulating, encouraging, and co-ordinating all the work being carried on by the seventy societies at present enrolled. Your committee are of opinion that further encouragement should be given to these societies and their individual working members by every means within the power of the Association ; and with the object of keeping the corresponding societies in more permanent touch with the Association they suggest that an official invitation on behalf of the Council be addressed to the societies, through the corresponding societies committee, asking them to appoint standing British Association sub-committees, to be elected by themselves, with the object of dealing with all those subjects of investigation common to their societies and to

the British Association committees, and to look after the general interests of science and scientific education throughout the provinces and provincial centres. . . .

"Your committee desire to lay special emphasis on the necessity for the extension of the scientific activity of the corresponding societies and the expert knowledge of many of their members in the direction of scientific education. They are of opinion that immense benefit would accrue to the country if the corresponding societies would keep this requirement especially in view with the object of securing adequate representation for scientific education on the Education Committees now being appointed under the new Act. The educational section of the Association having been but recently added, the corresponding societies have as yet not had much opportunity for taking part in this branch of the Association's work; and in view of the reorganisation in education now going on all over the country, your committee are of opinion that no more opportune time is likely to occur for the influence of scientific organisations to make itself felt as a real factor in national education. . . ."

I believe that if these suggestions or anything like them —for some better way may be found on inquiry—are accepted, great good to science throughout the Empire will come. Rest assured that sooner or later such a Guild will be formed because it is needed. It is for you to say whether it shall be, or form part of, the British Association. We in this Empire certainly need to organise science as much as in Germany they find the need to organise a navy. The German Navy League, which has branches even in our Colonies, already has a membership of 630,000, and its income is nearly £20,000 a year. A British Science League of 500,000 with a sixpenny subscription would give us £12,000 a year, quite enough to begin with.

I for one believe that the British Association would be a vast gainer by such an expansion of one of its existing functions. Increased authority and prestige would follow its increased utility. The meetings would possess a new interest; there would be new subjects for reports; missionary work less needed than formerly would be replaced by efforts much more suited to the real wants of the time. This magnificent, strong, and complicated organisation would become a living force, working throughout the year instead of practically lying idle, useless, and rusting for fifty-one weeks out of the fifty-two so far as its close association with its members is concerned.

If this suggestion in any way commends itself to you, then when you begin your work in your sections or General Committee see to it that a body is appointed to inquire how the thing can be done. Remember that the British Association will be as much weakened by the creation of a new body to do the work I have shown to have been in the minds of its founders as I believe it will be strengthened by becoming completely effective in every one of the directions they indicated, and for which effectiveness we, their successors, are indeed responsible. The time is appropriate for such a reinforcement of one of the wings of our organisation, for we have recently included Education among our sections.

There is another matter I should like to see referred to the committee I have spoken of, if it please you to appoint it. The British Association—which, as I have already pointed out, is now the chief body in the Empire which deals with the totality of science—is, I believe, the only organisation of any consequence which is without a charter, and which has not his Majesty the King as patron.

The First Work of such an Organisation.

I suppose it is my duty, after I have suggested the need of organisation, to tell you my personal opinion as to the matters where we suffer most in consequence of our lack of organisation at the present time.

Our position as a nation, our success as merchants, are in peril chiefly—dealing with preventable causes—because of our lack of completely efficient Universities and our neglect of research. This research has a double end. A professor who is not learning cannot teach properly or arouse enthusiasm in his students; while a student of anything who is unfamilar with research methods, and without that training which research brings, will not be in the best position to apply his knowledge in after-life. From neglect of research comes imperfect education, and a small output of new applications and new knowledge to re-invigorate our industries. From imperfect education comes the unconcern touching scientific matters, and the too frequent absence of the scientific spirit in the nation generally, from the Court to the Parish Council.

I propose to deal as briefly as I can with each of these points.

Universities.

I have shown that, so far as our industries are concerned, the cause of our failure has been run to earth; it is fully recognised that it arises from the insufficiency of our Universities both in numbers and efficiency, so that not only our captains of industry, but those employed in the nation's work generally, do not secure a training similar to that afforded by other nations. No additional endowment of primary, secondary, or technical instruction will mend matters. This is not merely the opinion of men of science; our great towns know it, our Ministers know it.

It is sufficient for me to quote Mr. Chamberlain:—

"It is not everyone who can, by any possibility, go forward into the higher spheres of education; but it is from those who do that we have to look for the men who in the future will carry high the flag of this country in commercial, scientific, and economic competition with other nations. At the present moment I believe there is nothing more important than to supply the deficiencies which separate us from those with whom we are in the closest competition. In Germany, in America, in our own colony of Canada, and in Australia, the higher education of the people has more support from the Government, is carried further than it is here in the Old Country; and the result is that in every profession, in every industry, you find the places taken by men and by women who have had a University education. And I would like to see the time in this country when no man should have a chance for any occupation of the better kind, either in our factories, our workshops, or our counting-houses, who could not show proof that in the course of his University career he had deserved the position that was offered to him. What is it that makes a country? Of course you may say, and you would be quite right, 'The general qualities of the people, their resolution, their intelligence, their pertinacity, and many other good qualities.' Yes; but that is not all, and it is not the main creative feature of a great nation. The greatness of a nation is made by its greatest men. It is those we want to educate. It is to those who are able to go, it may be, from the very lowest steps in the ladder, to men who are able to devote their time to higher education, that we have to look to continue the position which we now occupy as, at all events, one of the greatest nations on the face of the earth. And, feeling as I do on these subjects, you will not be surprised if I say that I think the time is coming when Governments will give more attention to this matter, and perhaps find a little more money to forward its interests."—(*Times*, November 6, 1902).

Our conception of a University has changed. University education is no longer regarded as the luxury of the rich, which concerns only those who can afford to pay heavily for it. The Prime Minister in a recent speech, while properly pointing out that the collective effect of our public and secondary schools upon British character cannot be overrated, frankly acknowledged that the boys of seventeen or eighteen who have to be educated in them "do not care a farthing about the world they live in, except in so far as it concerns the cricket-field or the football-field or the river." On this ground they are not to be taught science; and hence, when they proceed to the University, their curriculum is limited to subjects which were better taught before the modern world existed, or even Galileo was born

But the science which these young gentlemen neglect, with the full approval of their teachers, on their way through the school and the University to politics, the Civil Service, or the management of commercial concerns, is now one of the great necessities of a nation; and our Universities must become as much the insurers of the future progress as battleships are the insurers of the present power of States. In other words, University competition between States is now as potent as competition in building battleships; and it is on this ground that our University conditions become of the highest national concern, and therefore have to be referred to here, and all the more because our industries are not alone in question.

Why we have not more Universities.

Chief among the causes which have brought us to the terrible condition of inferiority as compared with other nations in which we find ourselves, are our carelessness in the matter of education, and our false notions of the limitations of State functions in relation to the conditions of modern civilisation.

Time was when the Navy was largely a matter of private and local effort. William the Conqueror gave privileges to the Cinque Ports on the condition that they furnished fifty-two ships when wanted. In the time of Edward III., of 730 sail engaged in the siege of Calais, 705 were "people's ships." All this has passed away; for our first line of defence we no longer depend on private and local effort.

Time was when not a penny was spent by the State on elementary education. Again, we no longer depend upon private and local effort. The Navy and primary education are now recognised as properly calling upon the public for the necessary financial support. But when we pass from primary to University education, instead of State endowment we find State neglect; we are in a region where it is nobody's business to see that anything is done.

We in Great Britain have thirteen Universities competing with 134 State and privately endowed in the United States, and twenty-two State endowed in Germany. I leave other countries out of consideration for lack of time, and I omit all reference to higher institutions for technical training, of which Germany alone possesses nine of University rank, because they are less important; they instruct rather than educate, and our want is education. The German State gives to one University more than the British Government allows to all the Universities and University Colleges in England, Ireland, Scotland, and Wales put together. These are the conditions which regulate the production of brain-power in the United States, Germany, and Britain respectively, and the excuse of the Government is that this is a matter for private effort. Do not our Ministers of State know that other civilised countries grant efficient State aid, and, further, that private effort has provided in Great Britain less than 10 per cent of the sum thus furnished in the United States in addition to State aid? Are they content that we should go under in the great struggle of the modern world because the Ministers of other States are wiser, and because the individual citizens of another country are more generous than our own?

If we grant that there was some excuse for the State's neglect so long as the higher teaching dealt only with words, and books alone had to be provided (for the streets of London and Paris have been used as class-rooms at a pinch), it must not be forgotten that during the last hundred years not only has knowledge been enormously increased, but things have replaced words, and fully equipped laboratories must take the place of books and class-rooms if University training worthy of the name is to be provided. There is much more difference in size and kind between an old and a new University than there is between the old caravel and a modern battleship, and the endowments must follow suit.

What are the facts relating to private endowment in this country? In spite of the munificence displayed by a small number of individuals in some localities, the truth must be spoken. In depending in our country upon this form of endowment we are trusting to a broken reed. If we take the twelve English University Colleges, the forerunners of Universities unless we are to perish from lack of knowledge, we find that private effort during sixty years has found less than £4,000,000; that is, £2,000,000 for buildings and £40,000 a year income. This gives us an average of £166,000 for buildings and £3300 for yearly income.

What is the scale of private effort we have to compete with in regard to the American Universities?

In the United States, during the last few years, Universities and colleges have received more than £40,000,000 from this source alone; private effort supplied nearly £7,000,000 in the years 1898-1900.

Next consider the amount of State aid to Universities afforded in Germany. The buildings of the new University of Strassburg have already cost nearly a million; that is, about as much as has yet been found by private effort for buildings in Manchester, Liverpool, Birmingham, Bristol, Newcastle, and Sheffield. The Government annual endowment of the same German University is more than £49,000.

This is what private endowment does for us in England, against State endowment in Germany.

But the State does really concede the principle; its present contribution to our Universities and colleges amounts to £155,600 a year. No capital sum, however, is taken for buildings. The State endowment of the University of Berlin in 1891-2 amounted to £168,777.

When, then, we consider the large endowments of University education both in the United States and Germany, it is obvious that State aid only can make any valid competition possible with either. The more we study the facts, the more statistics are gone into, the more do we find that we, to a large extent, lack both of the sources of endowment upon one or other, or both, of which other nations depend. We are between two stools, and the prospect is hopeless without some drastic changes. And first among these, if we intend to get out of the present Slough of Despond, must be the giving up of the idea of relying upon private effort.

That we lose most where the State does least is known to Mr. Chamberlain, for in his speech, to which I have referred, on the University of Birmingham, he said:—"As the importance of the aim we are pursuing becomes more and more impressed upon the minds of the people, we may find that we shall be more generously treated by the State."

Later still, on the occasion of a visit to University College School, Mr. Chamberlain spoke as follows:—

"When we are spending, as we are, many millions—I think it is £13,000,000—a year on primary education, it certainly seems as if we might add a little more, even a few tens of thousands, to what we give to University and secondary education."—(*Times*, November 6, 1902).

To compete on equal grounds with other nations we must have more Universities. But this is not all—we want a far better endowment of all the existing ones, not forgetting better opportunities for research on the part of both professors and students. Another crying need is that of more professors and better pay. Another is the reduction of fees; they should be reduced to the level existing in those countries which are competing with us—to, say, one-fifth of their present rates, so as to enable more students in the secondary and technical schools to complete their education.

In all these ways facilities would be afforded for providing the highest instruction to a much greater number of students. At present there are almost as many *professors and instructors* in the Universities and colleges of the United States as there are *day students* in the Universities and colleges of the United Kingdom.

Men of science, our leaders of industry, and the chiefs of our political parties all agree that our present want of higher education—in other words, properly equipped Universities—is heavily handicapping us in the present race for commercial supremacy, because it provides a rela-

tively inferior brain-power, which is leading to a relatively reduced national income.

The facts show that in this country we cannot depend upon private effort to put matters right. How about local effort?

Anyone who studies the statistics of modern municipalities will see that it is impossible for them to raise rates for the building and upkeep of Universities.

The buildings of the most modern Universities in Germany have cost a million. For upkeep the yearly sums found, chiefly by the State, for German Universities of different grades, taking the incomes of seven out of the twenty-two Universities as examples, are :—

First class ..	..	Berlin	£130,000
Second class	..	{Bonn / Göttingen} ..	56,000
Third class..	..	{Königsberg / Strassburg} ..	48,000
Fourth class	..	{Heidelberg / Marburg} ..	37,000

Thus, if Leeds, which is to have a University, is content with the fourth class German standard, a rate must be levied of 7d. in the pound for yearly expenses, independent of all buildings. But the facts are that our towns are already at the breaking strain. During the last fifty years, in spite of enormous increases in rateable values, the rates have gone up from about 2s. to about 7s. in the pound for real *local* purposes. But no University can be a merely local institution.

How to get more Universities.

What, then, is to be done? Fortunately, we have a precedent admirably in point, the consideration of which may help us to answer this question.

I have pointed out that in old days our Navy was chiefly provided by local and private effort. Fortunately for us those days have passed away; but some twenty years ago, in spite of a large expenditure, it began to be felt by those who knew, that in consequence of the increase of foreign navies our sea-power was threatened, as now, in consequence of the increase of foreign Universities, our brain-power is threatened.

The nation slowly woke up to find that its enormous commerce was no longer insured at sea, that in relation to foreign navies our own had been suffered to dwindle to such an extent that it was no longer capable of doing the duty which the nation expected of it even in times of peace. At first this revelation was received with a shrug of incredulity, and the peace-at-any-price party denied that anything was needed; but a great teacher arose;* as the facts were inquired into, the suspicion changed into an alarm; men of all parties saw that something must be done. Later, the nation was thoroughly aroused, and with an universal agreement the principle was laid down that, cost what it might to enforce our sea-power, our Navy must be made and maintained of a strength greater than those of any two possibly contending Powers. After establishing this principle, the next thing to do was to give effect to it. What did the nation do after full discussion and inquiry? A Bill was brought in in 1888, and a sum of £21,500,000 was voted in order, during the next five years, to inaugurate a large ship building programme, so that Britain and Britain's commerce might be guarded on the high seas in any event.

Since then we have spent £120,000,000 on new ships, and this year we spend still more millions on still more new ships. If these prove insufficient to safe-guard our sea-power, there is no doubt that the nation will increase them, and I have not heard that anybody has suggested an appeal to private effort.

How, then, do we stand with regard to Universities, recognising them as the chief producers of brain-power and therefore the equivalents of battleships in relation to sea-power? Do their numbers come up to the standard established by the Admiralty principle to which I have referred? Let us attempt to get a rough-and-ready estimate of our educational position by counting Universities as the Admiralty counts battleships. I say rough-and-ready, because we have other helps to greater brain-power to consider besides Universities, as the Admiralty has other ships to consider besides ironclads.

In the first place, let us inquire if they are equal in number to those of any two nations commercially competing with us.

In the United Kingdom we had until quite recently thirteen.* Of these, one is only three years old as a teaching University, and another is still merely an examining board.

In Germany there are twenty-two Universities; in France, under recent legislation, fifteen; in Italy, twenty-one. It is difficult to give the number in the United States, because it is clear, from the tables given in the Report of the Commissioner of Education, that some colleges are more important than some Universities, and both give the degree of Ph.D. But of Universities in title we have 134. Among these, there are forty-six with more than fifty professors and instructors, and thirteen with more than 150. I will take that figure.

Suppose we consider the United States and Germany our chief commercial competitors, and apply the Admiralty principle. We should require, allowing for population eight additional Universities at the very lowest estimate.

We see, then, that instead of having Universities equalling in number those of two of our chief competitors together, they are by no means equal to those of either of them singly.

After this statement of the facts, anyone who has belief in the importance of higher education will have no difficulty in understanding the origin of the present condition of British industry and its constant decline, first in one direction and then in another, since the tremendous efforts made in the United States and Germany began to take effect.

If, indeed, there be anything wrong about the comparison, the error can only arise from one of two sources—either the Admiralty is thoughtlessly and wastefully spending money, or there is no connection whatever between the higher intelligence and the prosperity of a nation. I have already referred to the views of Mr. Chamberlain and Lord Rosebery on this point; we know what Mr. Chamberlain has done at Birmingham; we know the strenuous efforts made by the commercial leaders of Manchester and Liverpool; we know, also, the opinion of men of science.

If while we spend so freely to maintain our sea-power our export of manufactured articles is relatively reduced because our competitors beat us in the markets of the world what is the end of the vista thus opened up to us? A Navy growing stronger every year and requiring larger votes to guard our commerce and communications, and a vanishing quantity of commerce to guard—a reduced national income to meet an increasing taxation!

The pity is that our Government has considered sea power alone; that while so completely guarding our commerce it has given no thought to one of the main conditions on which its production and increase depend. A glance could have shown that other countries were building Universities even faster than they were building battleships; were, in fact, considering brain-power first and sea power afterwards.

Surely it is my duty as your President to point out the danger ahead, if such ignoring of the true situation should be allowed to continue. May I express a hope that at

* Captain Mahan, of the U.S. Navy, whose book, "On the Influence of Sea-power on History," has suggested the title of my Address.

* These are Oxford, Cambridge, Durham, Victoria, Wales, Birmingham, London, St. Andrews, Glasgow, Aberdeen, Edinburgh, Dublin and Royal University.

last, in Mr. Chamberlain's words:—"The time is coming when Governments will give more attention to this matter?"

What will they Cost?

The comparison shows that we want eight new Universities, some of which, of course, will be colleges promoted to University rank, and fitted to carry on University work. Three of them are already named: Manchester, Liverpool, Leeds.

Let us take this number and deal with it on the battleship condition, although a modern University on American or German models will cost more to build than a battleship.

If our present University shortage be dealt with on battleship conditions, to correct it we should expend *at least* £8,000,000 for new construction, and for the pay-sheet we should have to provide (8 × £50,000) £400,000 yearly for *personnel* and up-keep; for it is of no use to build either ships or Universities without manning them. Let us say, roughly, capitalising the yearly payment at 2½ per cent, £24,000,000.

At this stage it is important to inquire whether this sum, arrived at by analogy merely, has any relation to our real University needs.

I have spent a year in making inquiries, as full as I could make them, of friends conversant with the real present needs of each of the Universities, old and new. I have obtained statistics which would fill a volume, and personally I believe that this sum at least is required to bring our University system up to anything like the level which is insisted upon both in the United States and in Germany. Even Oxford, our oldest University, will still continue to be a mere bundle of colleges unless three millions are provided to enable the University, properly so called, to take her place among her sisters of the modern world; and Sir Oliver Lodge, the Principal of our very youngest University, Birmingham, has shown in detail how five millions can be usefully and properly applied in that one locality to utilise for the good of the nation the enthusiasm and scientific capacity which are only waiting for adequate opportunity of development.

'How is this money to be raised? I reply, without hesitation, *Duplicate the Navy Bill of* 1888-9; do at once for brain-power what we so successfully did then for sea-power.

Let £24,000,000 be set apart from one asset, our national wealth, to increase the other, brain-power. Let it be assigned and borrowed as it is wanted; there will be a capital sum for new buildings to be erected in the next five or ten years, the interest of the remainder to go towards increased annual endowments.

There need be no difficulty about allocating money to the various institutions. Let each University make up its mind as to which rank of the German Universities it wishes to emulate. When this claim has been agreed to, the sums necessary to provide the buildings and teaching staff of that class of University should be granted without demur.

It is the case of battleships over again, and money need not be spent more freely in one case than in the other.

Let me at once say that this sum is not to be regarded as practically gone when spent, as in the case of a short-lived ironclad. *It is a loan* which will bear a high rate of interest. This is not my opinion merely; it is the opinion of those concerned in great industrial enterprises and fully alive to the origin and effects of the present condition of things.

I have been careful to point out that the statement that our industries are suffering from our relative neglect of science does not rest on my authority. But if this be true, then if our annual production is less by only two millions than it might have been, having two millions less to divide would be equivalent to our having forty or fifty millions less capital than we should have had if we had been more scientific.

Sir John Brunner, in a speech connected with the Liverpool School of Tropical Medicine, stated recently that if we as a nation were now to borrow ten millions of money in order to help science by putting up buildings and endowing professors, we should get the money back in the course of a generation a hundred-fold. He added that there was no better investment for a business man than the encouragement of science, and that every penny he possessed had come from the application of science to commerce.

According to Sir Robert Giffen, the United Kingdom as a going concern was in 1901 worth £16,000,000,000.

Were we to put aside £24,000,000 for gradually organising, building, and endowing new Universities, and making the existing ones more efficient, we should still be worth £15,976,000,000—a property well worth defending by all the means, and chief among these brain-power, we can command.

If it be held that this, or anything like it, is too great a price to pay for correcting past carelessness or stupidity, the reply is that the £120,000,000 recently spent on the Navy, a sum five times greater, has been spent to correct a sleepy blunder, not one whit more inimical to the future welfare of our country than that which has brought about our present educational position. We had not sufficiently recognised what other nations had done in the way of ship-building, just as until now we have not recognised what they have been doing in University building.

Further, I am told that the sum of £24,000,000 is less than half the amount by which Germany is yearly enriched by having improved upon our chemical industries, owing to our lack of scientific training. Many other industries have been attacked in the same way since; but taking this one instance alone, if we had spent this money fifty years ago, when the Prince Consort first called attention to our backwardness, the nation would now be much richer than it is, and would have much less to fear from competition.

Suppose we were to set about putting our educational house in order, so as to secure a higher quality and greater quantity of brain-power, it would not be the first time in history that this has been done. Both Prussia after Jena and France after Sedan acted on the view—

> "When land is gone and money spent,
> Then learning is most excellent."

After Jena, which left Prussia a "bleeding and lacerated mass," the King and his wise counsellors, among them men who had gained knowledge from Kant, determined, as they put it, "to supply the loss of territory by intellectual effort."

What did they do? In spite of universal poverty, three Universities, to say nothing of observatories and other institutions, were at once founded, secondary education was developed, and in a few years the mental resources were so well looked after that Lord Palmerston defined the kingdom in question as "a country of damned professors."

After Sedan—a battle, as Moltke told us, "won by the schoolmaster"—France made even more strenuous efforts. The old University of France, with its "academies" in various places, was replaced by fifteen independent Universities, in all of which are faculties of letters, sciences, law, and medicine.

The development of the University of Paris has been truly marvellous. In 1897-8 there were 12,000 students, and the cost was £200,000 a year.

But even more wonderful than these examples is the "intellectual effort" made by Japan, not after a war, but to prepare for one.

The question is—Shall we wait for a disaster and then imitate Prussia and France; or shall we follow Japan and thoroughly prepare by "intellectual effort" for the industrial struggle which lies before us?

Such an effort seems to me to be the first thing any national or imperial scientific organisation should endeavour to bring about.

(To be continued).

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 99).

Chapter II.

Method of Research.

The results of the investigation of radio-active minerals, announced in the preceding chapter, led M. Curie and myself to endeavour to extract a new radio-active body from pitchblende. Our method of procedure could only be based on radio-activity, as we know of no other property of the hypothetical substance. The following is the method pursued for a research based on radio-activity :—The radio-activity of a compound is determined, and a chemical decomposition of this compound is effected ; the radio-activity of all the products obtained is determined, having regard to the proportion in which the radio-active substance is distributed among them. In this way, an indication is obtained, which may to a certain extent be compared to that which spectrum analysis furnishes. In order to obtain comparable figures, the activity of the substances must be determined in the solid form well dried.

Polonium, Radium, Actinium.

The analysis of pitchblende, with the help of the method just explained, led us to the discovery in this mineral of two strongly radio-active substances, chemically dissimilar : —Polonium, discovered by ourselves, and radium, which we discovered in conjunction with M. Bémont.

Polonium, from the analytical point of view, is analogous to bismuth, and separates out with the latter. By one of the following methods of fractionating, bismuth products are obtained increasingly rich in polonium :—

1. Sublimation of the sulphides *in vacuo ;* the active sulphide is much more volatile than bismuth sulphide.

2. Precipitation of solutions of the nitrates by water ; the precipitate of the basic nitrate is much more active than the salt which remains in solution.

3. Precipitation by sulphuretted hydrogen of a hydrochloric acid solution, strongly acid ; the precipitated sulphides are considerably more active than the salt which remains in solution.

Radium is a substance which accompanies the barium obtained from pitchblende ; it resembles barium in its reactions, and is separated from it by difference of solubility of the chlorides in water, in dilute alcohol, or in water acidified with hydrochloric acid. We effect the separation of the chlorides of barium and radium by subjecting the mixture to fractional crystallisation, radium chloride being less soluble than that of barium.

A third strongly radio-active body has been identified in pitchblende by M. Debierne, who gave it the name of *actinium*. Actinium accompanies certain members of the iron group contained in pitchblende ; it appears in particular allied to thorium, from which it has not yet been found possible to separate it. The extraction of actinium from pitchblende is a very difficult operation, the separations being as a rule incomplete.

All three of the new radio-active bodies occur in quite infinitesimal amount in pitchblende. In order to obtain them in a more concentrated condition, we were obliged to treat several tons of residue of the ore of uranium. The rough treatment was carried out in the factory ; and this was followed by processes of purification and concentration. We thus succeeded in extracting from thousands of kilogrms. of crude material a few decigrammes of products which were exceedingly active as compared with the ore from which they were obtained. It is obvious that this process is long, arduous, and costly.

Other new radio-active bodies have been notified since the termination of our work. M. Giesel, on the one hand, and MM. Hoffmann and Strauss on the other, have announced the probable existence of a radio-active body similar to lead in its chemical properties. At present only a few samples of this substance have been obtained.

Radium is, so far, the only member of the new radio-active substances that has been isolated as the pure salt.

Spectrum of Radium.

It was of the first importance to check, by all possible means, the hypothesis, underlying this work, of new radio-active elements. In the case of radium, spectrum analysis was the means of confirming this hypothesis.

M. Demarçay undertook the examination of the new radio-active bodies by the searching methods which he employs in the study of photographic spark spectra.

The assistance of so competent a scientist was of the greatest value to us, and we are deeply grateful to him for having consented to take up this work. The results of the spectrum analysis brought conviction to us when we were still in doubt as to the interpretation of the results of our research.

The first specimens of fairly active barium chloride containing radium, examined by M. Demarçay, exhibited together with the barium lines a new line of considerable intensity and of wave-length $\lambda = 381{\cdot}47\ \mu\mu$ in the ultra-violet. With the more active products prepared subsequently, Demarçay saw the line $381{\cdot}47\ \mu\mu$ more distinctly ; at the same time other new lines appeared, and the intensity of the new lines was comparable with that of the barium lines. A further concentration furnished a product for which the new spectrum predominated, and the three strongest barium lines, alone visible, merely indicated the presence of this metal as an impurity. This product may be looked upon as nearly pure radium chloride. Finally, by further purification, I obtained an exceedingly pure chloride, in the spectrum of which the two chief barium lines were scarcely visible.

The following is a list, according to Demarçay, of the principal radium lines for the portion of the spectrum included between $\lambda = 500{\cdot}0$ and $\lambda = 350{\cdot}0\ \mu\mu$. The intensity of each line is represented by a figure, the strongest being marked 16 :—

λ.	Intensity.	λ.	Intensity.
482·63	10	460·03	3
472·69	5	453·35	9
469·98	3	443·61	8
469·21	7	434·06	12
468·30	14	381·47	16
464·19	4	364·96	12

All the lines are clear and narrow, the three lines 381·47, 468·30, 434·06 are strong, and equal the most intense of those actually known. Two well-marked misty bands are also visible in the spectrum. The first, which is symmetrical, extends from 463·10 to 462·19, with a maximum at 462·75. The second, which is stronger, fades towards the ultra-violet ; it begins, sharply defined, at 446·37, and passes through a maximum at 445·52 ; the region of the maximum extends as far as 445·34, then a nebulous band, gradually fading, extends about as far as 439.

In the least refrangible part, not photographed in the spark spectrum, the only significant line is 566·5 (approx.), much more feeble, however, than 482·63.

The general aspect of the spectrum is that of the metals of the alkaline earths ; these metals are known to have well-marked line spectra with certain nebulous bands.

According to Demarçay, the position of radium may be among the bodies possessing the most sensitive spectrum reaction. I also have concluded from the work of concentration, that in the first specimen examined, which showed clearly the line 3814·7, the proportion of radium must have been very small (perhaps about 0·02 per cent). Nevertheless, an activity fifty times as great as that of metallic uranium is required in order to distinguish clearly the principal radium line in the spectra photographed. With a sensitive electrometer the radio-activity of a substance only $\frac{1}{100}$ of that of metallic uranium can be detected. It is clear that, in order to detect the presence

* Thesis presented to the Faculté des Sciences de Paris.

of radium, the property of radio-activity is several thousand times more sensitive than the spectrum reaction.

Bismuth containing polonium and thorium containing actinium, both very active, examined by Demarçay, have so far each only yielded bismuth and thorium lines.

In a recent publication, M. Giesel, who is occupied in preparing radium, states that radium bromide gives a carmine flame colouration. The flame spectrum of radium contains two beautiful red bands, one line in the blue-green, and two faint lines in the violet.

Extraction of the New Radio-active Substances.

The first stage of the operation consists in extracting barium with radium from the ores of uranium, also bismuth with polonium and the rare earths containing actinium from the same. These three primary products having been obtained, the next step is in each case to endeavour to isolate the new radio-active body. This second part of the treatment consists of a process of fractionation. The difficulty of finding a very perfect means of separating closely allied elements is well known ; methods of fractionation are therefore quite suitable. Besides this, when a mere trace of one element is mixed with another element, no method of complete separation could be applied to the mixture, even allowing that such a method was known ; in fact, one would run the risk of losing the trace of the material to be separated.

The particular object of my work has been the isolation of radium and polonium. After working for several years, I have so far only succeeded in obtaining the former.

Pitchblende is an expensive ore, and we have given up the treatment of it in large quantities. In Europe the extraction of this ore is carried out in the mine of Joachimsthal, in Bohemia. The crushed ore is roasted with carbonate of soda, and the resulting material washed, first with warm water and then with dilute sulphuric acid. The solution contains the uranium, which gives pitchblende its value. The insoluble residue is rejected. This residue contains radio-active substances ; its activity is four and a-half times that of metallic uranium. The Austrian Government, to whom the mine belongs, presented us with a ton of this residue for our research, and authorised the mine to give us several tons more of the material.

It was not very easy to apply the methods of the laboratory to the preliminary treatment of the residue in the factory. M. Debierne investigated this question, and organised the treatment in the factory. The most important point of his method is the conversion of the sulphates into carbonate by boiling the material with a concentrated solution of sodium carbonate. This method avoids the necessity of fusing with sodium carbonate.

The residue chiefly contains the sulphates of lead and calcium, silica, alumina, and iron oxide. In addition nearly all the metals are found in greater or smaller amount (copper, bismuth, zinc, cobalt, manganese, nickel, vanadium, antimony, thallium, rare earths, niobium, tantalum, arsenic, barium, &c.). Radium is found in this mixture as sulphate, and is the least soluble sulphate in it. In order to dissolve it, it is necessary to remove the sulphuric acid as far as possible. To do this, the residue is first treated with a boiling concentrated soda solution. The sulphuric acid combined with the lead, aluminium, and calcium passes, for the most part, into solution as sulphate of sodium, which is removed by repeatedly washing with water. The alkaline solution removes at the same time lead, silicon, and aluminium. The insoluble portion is attacked by ordinary hydrochloric acid. This operation completely disintegrates the material, and dissolves most of it. Polonium and actinium may be obtained from this solution ; the former is precipitated by sulphuretted hydrogen, the latter is found in the hydrates precipitated by ammonia in the solution separated from the sulphides and oxidised. Radium remains in the insoluble portion. This portion is washed with water, and then treated with a boiling concentrated solution of carbonate of soda. This operation completes the transformation of the sulphates of barium and radium into carbonates. The material is then thoroughly washed with water, and then treated with dilute hydrochloric acid, quite free from sulphuric acid. The solution contains radium as well as polonium and actinium. It is filtered and precipitated with sulphuric acid. In this way the crude sulphates of barium containing radium and calcium, of lead, and of iron, and of a trace of actinium are obtained. The solution still contains a little actinium and polonium, which may be separated out as in the case of the first hydrochloric acid solution.

From one ton of residue 10 to 20 kilogrms. of crude sulphates are obtained, the activity of which is from thirty to sixty times as great as that of metallic uranium. They must now be purified. For this purpose they are boiled with sodium carbonate and transformed into the chlorides. The solution is treated with sulphuretted hydrogen, which gives a small quantity of active sulphides containing polonium. The solution is filtered, oxidised by means of chlorine, and precipitated with pure ammonia. The precipitated hydrates and oxides are very active, and the activity is due to actinium. The filtered solution is precipitated with sodium carbonate. The precipitated carbonates of the alkaline earths are washed and converted into chlorides. These chlorides are evaporated to dryness, and washed with pure concentrated hydrochloric acid. Calcium chloride dissolves almost entirely, whilst the chloride of barium and radium remains insoluble. Thus, from one ton of the original material about 8 kilogrms. of barium and radium chloride are obtained, of which the activity is about sixty times that of metallic uranium. The chloride is now ready for fractionation.

(To be continued).

ALUMINIUM THE CHIEF INORGANIC ELEMENT IN A PROTEACEOUS TREE, AND THE OCCURRENCE OF ALUMINIUM SUCCINATE IN TREES OF THIS SPECIES.*

By HENRY G. SMITH, F.C.S.,
Assistant Curator, Technological Museum, Sydney.

In this paper the author announces the discovery of a flowering plant which uses the element aluminium in large quantities in its construction, and thus differs in this respect from all other Phanerogams. This plant, *Orites excelsa*, R. Br., (N.O. Proteaceæ) is one of the "Silky Oaks" of Australia, and occurs plentifully in northern New South Wales and Queensland. It is a tall tree, and reaches a diameter of three feet. A section of a tree from Queensland was exhibited which was three feet in diameter. In the centre of this tree was a large deposit of a basic aluminium succinate of the formula $Al_2(C_4H_4O_4)_3Al_2O_3$. The ash of the wood furthest from the deposit contained 79·61 per cent of alumina, a considerably larger amount than had previously been found in any of the Cryptogams, in which alone aluminium was supposed to occur. This specimen was evidently an abnormal one in regard to the large amount of alumina, and the deposit of aluminium succinate is evidently nature's method of getting rid of an excess of aluminium. Three other samples of the trees of this species from northern New South Wales were investigated, and in the ash of all these large quantities of alumina was found, ranging in amount from 36 to 43 per cent. A large amount of the alumina in the ash was present as an aluminate of potash soluble in water, and as no carbonate of potash was detected it is supposed that the potassium aluminate was originally present in the tree as such. In the ash of the sample from Mullimbimby, cobalt was found, together with 3 per cent of manganese, so that probably cobaltiferous manganese occurs in that locality. Free normal butyric acid was found in the succinate

* A Paper read before the Royal Society of New South Wales, July 1, 1903,

deposit; this was separated and determined by its barium salt; no other volatile acid could be detected. It is evident that the succinic acid is derived from the butyric acid by natural oxidation, and it then probably forms the basic salt with the aluminium in solution. Investigation was made of the ash of *Grevillea robusta*, of *G. Hilliana*, and of *G. striata*, but no alumina could be detected in either, so that the statement previously made (*Proc. Roy. Soc. N.S.W.*, 1895) that aluminium succinate occurred in the timber of *Grevillea robusta* was evidently made in error, and it is probable that the tree from which that deposit was obtained was *Orites excelsa*. When portions of the wood of the Queensland sample were ignited, it was possible to obtain the characteristic cobalt-blue colour for alumina when the ash was moistened with cobalt nitrate and ignited, the other salts being too small in amount to interfere with the reaction.

NOTE ON THE

ESTIMATION OF SILICON IN FORGE-IRON.

By GEORGE FREDERICK HORSLEY.

The great disadvantage of the ordinary nitro-sulphuric acid process for the estimation of silicon in forge-iron lies in the liability towards explosive spurting—at least, this is my experience—towards the end of the preliminary evaporation to dryness. There is also an occasional tendency towards the formation of gelatinous silica. Experiments were therefore made, using various proportions of the three common acids, until a process was devised which is free from both these objections, and which I trust is not well-known already to all my readers.

To 1 grm. of forge-iron add 10 c.c. of dilute H_2SO_4 (1 part acid to 4 parts water) and 15 c.c. of HCl. Boil down till fumes of SO_3 are evolved. Cool, add 100 c.c. water and 10 c.c. HCl, and boil. Filter, and wash once with 5 c.c. HCl and four times with hot water. Dry and ignite.

NOTICES OF BOOKS

The Alchemist. By Ben Jonson. Edited, with Introduction, Notes, and Glossary, by Charles Montgomery Hathaway, jun., Ph.D. New York: Henry Holt and Co. 1903.

This reprint of Ben Jonson's famous play will owe its interest in the eyes of chemists chiefly to the interesting exposition of the theory and practice of alchemy, which precedes the text; in this description of the predecessor of modern scientific chemistry, its origin, sources, and abuses are fully detailed, with much that is both amusing and instructive with regard to its relations to medicine, astrology, palmistry, and to "all sorts of swindling operations"; in this connection are to be found some astonishing facts relating to modern attempts at deluding the ignorant public into belief in gold-making swindles. The text of the Alchemist, which is that of the folio of 1616, is fully annotated with explanatory notes, and well repays critical analysis by the lights it throws on the practices of those who may be regarded as the first chemical investigators.

Grundriss der Reinen und Angewandten Elektrochemie. ("Outlines of Pure and Applied Electrochemistry"). By P. Ferchland, Dr.Phil. Halle-a-S.: Wilhelm Knapp. 1903.

The author of this book states in the preface that in writing it he had in view chiefly the needs of advanced students who already possess a fairly considerable knowledge of physics and chemistry. Such being the case, some parts of the description of simple apparatus and elementary methods, which are always to be found in first text-books of electricity, might well have been omitted as likely to be perfectly well known by the reader; it appears probable also that it would have been better to introduce the chapters on the theory of solutions and osmotic pressure rather earlier in the volume; but apart from these two points, there is very little to be criticised unfavourably, and on the whole the work may be thoroughly recommended. Though covering much the same ground as many similar works, it has the advantage of being written in a more than usually interesting style, and the striking language of some of the explanations will tend to assist greatly the memory of the student. The illustrations are exceedingly diagrammatic, but both clear and accurate. It is to be regretted that the section on applied electrochemistry is not fuller, some thirty pages only dealing with this branch of the subject.

Selbststrahlende Materie, Atome, und Elektronen. ("Radiant Matter, Atoms, and Electrons"). By Privatdocent Dr. Paul Köthner. Berlin: Julius Springer.

This paper, which is a reprint from the *Zeitschrift für Angewandte Chemie*, describes somewhat briefly and in an elementary manner the phenomena of radio-activity, and the recent work of Becquerel, Rutherford, the Curies, and others, with copious references to original publications. Those who have not followed the astonishingly rapid developments of our knowledge of radio-activity will find this summary convenient for use as a basis for further study; at the same time, a greater insistence on the quantitative results which have been obtained would greatly add to its value for all purposes. Though containing nothing absolutely new, the critical examinations of the various theories put forward are unbiassed and thoughtful, especially as regards Rutherford's views, with which the author does not always find himself in agreement. Such a paper as this must necessarily have only a more than usually transitory value, but at the same time an occasional review of the present standpoint will certainly be helpful to those who are following with interest the investigations of others, and possibly may suggest new lines of thought or experiment to these latter.

Die Herstellung der Akkumulatoren. ("The Production of Accumulators"). By F. Grünwald. Halle-a-S.: Wilhelm Knapp. 1903.

The third edition of this handy little book has been brought up to date and made more complete, some parts having been entirely re-written for this purpose. The great advances recently made in the manufacture of accumulators are fully described, with a considerable amount of information relating to the raw materials used for making lead accumulators, their management and applications. There is in places rather a suggestion of the adoption of rule-of-thumb precepts and methods, and the lack of a good index seriously impairs the usefulness of the book, but it appears to give a very full account of the subject, and is well illustrated. A few tables of specific resistance, and the specific gravity and percentage composition of sulphuric acid, &c., are to be found in the appendix.

Elementare Vorlesungen uber Telegraphie und Telephonie. 4 Lieferung. ("Elementary Lectures on Telegraphy and Telephony." Part IV.). By Dr. Richard Heilbrun. Berlin: Georg Siemens. 1902.

This number of Dr. Heilbrun's Elementary Lectures brings to a conclusion the general part, which is supposed to give students sufficient insight into the more purely scientific sides of physics and chemistry to enable them to understand the theory of telegraphy. In the eleventh lecture rather a sketchy account is given of some of the most important facts of the science of Sound, and the twelfth lecture proceeds to the description of the Morse alphabet and the various modifications of telegraphic apparatus. The previous lectures have already been reviewed in these columns, and there appears nothing to add to, or alter in, the views already expressed.

CHEMICAL NOTICES FROM FOREIGN SOURCES

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 5, August 3, 1903.

Double Carbide of Chromium and Tungsten.—Henri Moissan and A. Kouznetzow.—The authors prepare by different processes a double carbide of chromium and tungsten of formula $W_2C.3Cr_3C_2$. This double carbide is comparable with the analogous compounds found by MM. Carnot and Goutal in siderurgical products. Its density is 8·41. It is a very stable carbide, and is not attacked by acids and the principal reagents, and is remarkable for its extreme hardness. This latter fact leads the authors to the conclusion that the addition of tungsten to chromated steels may possibly cause the formation of this product, and at the same time produce new and special properties in the steels.

Transformations of Aldehydes and Ketones into Alcohols by Catatylic Hydrogenation.—Paul Sabatier and J. B. Senderens.—The direct action of hydrogen in presence of nickel allows of the easy transformation of formenic aldehydes and ketones into the corresponding alcohols. This method has the great advantages over the usual process (action of sodium or sodium amalgam in presence of water)—(1) that there is no accessory product such as pinacone, and (2) during the first process a very good yield of the alcohol is given. The catalytic properties of metals can be employed for the two inverse reactions. On the one hand, reduced copper causes the cleavage of alcohols into hydrogen and aldehydes or ketones, and on the other hand, nickel, in presence of hydrogen at a lower temperature, transforms these latter substances into alcohol.

Estimation of Pyridine in Aqueous Solution.—Maurice François.—The author estimates pyridine in aqueous solution by adding to the solution ready for titration an excess of solution of iodine in potassium iodide, and titrating the iodine left in solution after the deposition of the pyridine periodide. He finds, however, that this method is not very accurate, the pyridine not being entirely precipitated. If, however, he estimates pyridine in the state of the chloraurate very good results are obtained. The details of this estimation are given.

Secondary Amides.—M. Tarbouriech.—The introduction into the molecule of a second radicle causes propionamide to lose the basic character which enables all the primary amides to combine with certain metallic chlorides and picric acid. In the presence of mineral acids the dipropionamide is rapidly hydrolysed with transformation into an ammonia salt.

Reduction of the Ether Salts of Acids of Complex Function.—L. Bouveault and G. Blanc.—The authors reduce the ether salts of non-saturated acids, acid-alcohols, β-ketonic acids, and bibasic acids by means of sodium and absolute alcohol.

Action of Phenylhydrazine on Alcoholic Bromides and Iodides.—J. Allain Le Canu.—Even in alcoholic solution, ethyl bromide can form the bibasic bromhydrate of phenylhydrazine. At the same time, the monobasic bromhydrate and a neutral salt, diethyl bromide of phenylhydrazine, is formed. The same reaction occurs with the iodides of methyl and ethyl, which, with iodides of a higher order, give, in the first place, tribasic iodohydrate of phenylhydrazine. The author also gives the preparation and describes the properties of dipropyl- and diamylphenylhydrazine.

Thermochemical Researches on Colouring Matters; Rosaniline and Pararosaline.—Jules Schmidlin.—The author makes a series of thermochemical researches on the phenomena of neutralisation of colouring matters, and so contributes to the properties of colouring matters in general and of rosaniline and pararosaniline in particular. The slight solubility of rosaniline and its salts necessitates the researches being made with very dilute solutions.

MISCELLANEOUS.

Schools of Chemistry, &c.—The following additional information of interest to Students has been received :—

Northern Polytechnic Institute, Holloway Road, N.—Head of Chemical Department, Dr. W. H. Mills. Assistants, Mr. W. H. Watson, B.Sc., A.R.C.S., Miss M. A. Bain, M.A., B.Sc., Mr. F. E. Grant, B.Sc. Lectures and Practical Classes in Elementary, Advanced, and Honours Inorganic and Organic Chemistry are held in the evenings from 7 p.m. to 10 p.m., affording instruction in the Courses for the Examinations of the University of London and the Board of Education. The Classes form a Course of Study extending over five Sessions, and are open to both sexes. Large new laboratories and lecture rooms have this Session been added to the Chemical Department, and every facility is afforded for advanced study and research. A reference library is attached to the Chemical Department. Session begins September 22.

Redruth School of Mines, Cornwall.—Principal, Mr. Howard C. Ridding, A.R.S.M., F.I.C.; Vice-Principal, Mr. T. Collins. Chemistry, Assaying, Mineralogy, Magnetism, and Electricity: The Principal. Practical Mining: Capt. W. Hambly, M.E. Mine and Land Surveying, Mechanics, and Geology: Mr. R. H. Watson, B.A., and Mr. R. A. H. Urquhart. Mathematics: Mr. T. Shopland, B.A. Principles of Mining, Ore Dressing, and Technical Drawing: Mr. F. H. Michell, C.E. Steam and Machine Construction and Drawing: Mr. Joseph Blight. Secretary and Registrar: Mr. James A. Winn.

Action of Fused Potash on Fluorene. Synthesis of *o*-Phenylbenzoic Acid.—M. Weger and K. Doring.—The authors have observed that when fluorene is treated with potash infusion for several hours, a small quantity of acid is formed, which they recognise as *o*-phenylbenzoic acid; the amount increases as the duration of the time of fusion is longer. This acid, which is obtained from the alkaline filtrate by the addition of sulphuric acid, should be boiled several times with water, to free it from a brown resin present in small quantity. It then separates out in the form of microscopic crystals, fusible at 113·5—114·5°; this acid is very difficultly soluble in water, but is easily soluble in alcohol, benzene, xylene, and glacial acetic acid. Its copper salt is anhydrous, and corresponds to the formula $(C_{13}H_9O_2)_2$ Cu. The acid dissolves easily in the cold, in concentrated sulphuric acid, giving a red colour water precipitates the yellow biphenylene-ketone (fluorenone) directly from this solution; it is fusible at 83—84°. The secondary reaction which takes place when we melt fluorene with potash, can be expressed by the following equation—

$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CH_2 + KOH + H_2O = \begin{matrix} C_6H_5 \\ | \\ C_6H_4COOK \end{matrix} + 2H_2.$$

The elimination of hydrogen has been proved. This observation explains why in fusing fluorene with caustic potash, we are able to obtain chemically-pure fluorene, but not fluorene-potassium in the same state; it is for the purpose of confirming the phenomenon that the authors undertook the closer examination of the action of melted potash on fluorene. They found also in the fluorene prepared by the method of fusion with potash, a small quantity of phenanthrene.—*Berichte*, vol. xxxvi., p. 878.

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2286.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Southport, 1903.

INAUGURAL ADDRESS OF THE PRESIDENT,

Sir Norman Lockyer, K.C.B., LL.D., F.R.S.,
Correspondant de l'Institut de France.

(Concluded from p. 133).

Research.

When dealing with our Universities I referred to the importance of research, as it is now generally acknowledged to be the most powerful engine of education that we possess. But education, after all, is but a means to the end, which, from the national point of view, is the application of old and the production of new knowledge.

Its national importance apart from education is now so generally recognised that in all civilised nations except our own means of research are being daily more amply provided for all students after they have passed through their University career; and, more than this, for all who can increase the country's renown or prosperity by the making of new knowledge, upon which not only commercial progress, but all intellectual advance must depend.

I am so anxious that my statement of our pressing, and indeed imperative, needs in this direction should not be considered as resting upon the possibly interested opinion of a student of science merely that I must trouble you with still more quotations.

Listen to Mr. Balfour :—

"I do not believe that any man who looks round the equipment of our Universities or medical schools or other places of education can honestly say in his heart that we have done enough to equip research with all the costly armoury which research must have in these modern days. We, the richest country in the world, lag behind Germany, France, Switzerland, and Italy. Is it not disgraceful? Are we too poor or are we too stupid? (*Nature*, May 30, 1901).

It is imagined by many who have given no thought to the matter that this research should be closely allied with some application of science being utilised at the time. Nothing could be further from the truth; nothing could be more unwise than such a limitation.

Surely all the laws of Nature will be ultimately of service, and therefore there is much more future help to be got from a study of the unknown and the unused than we can hope to obtain by continuing the study of that which is pretty well known and utilised already. It was a King of France, Louis XIV., who first commended the study of the *même inutile*. The history of modern science shows us more and more as the years roll on the necessity and advantage of such studies, and therefore the importance of properly endowing them; for the production of new knowledge is a costly and unremunerative pursuit.

Years ago we had Faraday apparently wasting his energies and time in playing with needles; electricity now fills the world. To-day men of science in all lands are studying the emanations of radium; no research could be more abstract; but who knows what advance in human thought may follow or what gigantic world-transforming superstructure may eventually be raised on the minute foundation they are laying?

If we so organise our teaching forces that we can use them at all stages, from the gutter to the University, to sift out for us potential Faradays—to utilise the mental products which otherwise would be wasted—it is only by enabling such men to continue their learning after their teaching is over that we shall be able to secure the greatest advantage which any educational system can afford.

It is now more than thirty years ago that my attention was specially drawn to this question of the endowment of research—first, by conversations with M. Dumas, the permanent secretary of the Academy of Sciences, who honoured me by his friendship; and, secondly, by my association with Sir Benjamin Brodie and Dr. Appleton in their endeavours to call attention to the matter in this country. At that time a general scheme of endowment suggested by Dumas was being carried out by Duruy. This took the form of the "Ecole spéciale des Hautes Études"; it was what our fellowship system was meant to be—an endowment of the research of post-graduate students in each seat of learning. The French effort did not begin then.

I may here tell, as it was told me by Dumas, the story of Léon Foucault, whose many discoveries shed a glory on France and revived French industry in many directions (see *Proc. Roy. Soc.*, vol. xvii., p. lxxxiii.). In 1851, when Prince Napoleon was President of the Republic, he sent for Dumas and some of his colleagues, and told them that during his stay in England, and afterwards in his study of the Great Exhibition of that year, he had found there a greater industrial development than in France, and more applications of science, adding that he wished to know how such a state of things could be at once remedied. The answer was that new applications depended upon new knowledge, and that therefore the most direct and immediate way was to find and encourage men who were likely by research in pure science to produce this new knowledge. The Prince-President at once asked for names; that of Léon Foucault was the only one mentioned during the first interview.

Some time afterwards—to be exact, at about eleven in the morning of December 2—Dumas's servant informed him that there was a gentleman in the hall named Foucault, who wished to see him, and he added that he appeared to be very ill. When shown into the study, Foucault was too agitated to speak, and was blind with tears. His reply to Dumas's soothing questions was to take from his pockets two rolls of banknotes, amounting to 200,000 francs, and place them on the table. Finally, he was able to say that he had been with the Prince-President since eight o'clock that morning, discussing the possible improvement of French science and industry; and that Napoleon had finally given him the money, requesting him to do all in his power to aid the State. Foucault ended by saying that, on realising the greatness of the task thus imposed upon him, his fears and feelings had got the better of him, for the responsibility seemed more than he could bear.*

The movement in England to which I have referred began in 1872, when a society for the organisation of academical study was formed in connection with the inquiry into the revenues of Oxford and Cambridge, and there was a famous meeting at the Freemasons' Tavern, Mark Pattison being in the chair. Brodie, Rolleston, Carpenter, Burdon-Sanderson, were among the speakers, and the first resolution carried was, "That to have a class of men whose lives are devoted to research is a national object." The movement died in consequence of the want of sympathy of the University authorities (see *Nature*, November and December, 1872).

In the year 1874, the subject was inquired into by the

* In order to show how history is written, what actually happened on a fateful morning may be compared with the account given by Kinglake :—"Prince Louis rode home and went in out of sight. Then for the most past he remained close shut up in the Elysée. There, in an inner room, still decked in red trousers, but with his back to the daylight, they say he sat bent over a fireplace for hours and hours together, resting his elbows on his knees, and burying his face in his hands."—"Crimean War," vol. i., p. 245.

late Duke of Devonshire's Commission; and after taking much remarkable evidence, including that of Lord Salisbury, the Commission recommended to the Government that the then grant of £1000, which was expended, by a committee appointed by the Royal Society, on instruments needed in researches carried on by private individuals, should be increased, so that personal grants should be made. This recommendation was accepted and acted on; the grant was increased to £4000, and, finally, other societies were associated with the Royal Society in its administration. The committee, however, was timorous, possibly owing to the apathy of the Universities, and the general carelessness on such matters, and only one personal grant was made; the whole conception fell through.

Meantime, however, opinion has become more educated and alive to the extreme importance of research to the nation, and in 1891, a suggestion was made to the Royal Commission which administers the proceeds of the 1851 Exhibition that a sum of about £6000 a year available for scholarships should be employed in encouraging post-graduate research throughout the whole Empire. As what happened is told in the Memoirs of Lord Playfair, it is not indiscreet in me to state that when I proposed this new form of the endowment of research it would not have surprised me if the suggestion had been declined. It was carried through by Lord Playfair's enthusiastic support. This system has been at work ever since, and the good that has been done by it is now generally conceded.

It is a supreme satisfaction to me to know that in this present year of grace the national importance of the study of the *même inutile* is more generally recognised than it was during the times to which I have referred in my brief survey; and, indeed, we students are fortunate in having on our side in this matter two members of His Majesty's Government, who two years ago spoke with no uncertain sound upon this matter:—

"Do we lack the imagination required to show what these apparently remote and abstract studies do for the happiness of mankind? We can appreciate that which obviously and directly ministers to human advancement and felicity, but seem, somehow or another, to be deficient in that higher form of imagination, in that longer sight, which sees in studies which have no obvious, necessary, or immediate result the foundation of the knowledge which shall give far greater happiness to mankind than any immediate, material, industrial advancement can possibly do; and I fear, and greatly fear, that, lacking that imagination, we have allowed ourselves to lag in the glorious race run now by civilised countries in pursuit of knowledge, and we have permitted ourselves so far to too large an extent to depend upon others for those additions to our knowledge which surely we might have made for ourselves" (Mr. Balfour, *Nature*, May 30, 1901).

"I would remind you that all history shows that progress—national progress of every kind—depends upon certain individuals rather than upon the mass. Whether you take religion, or literature, or political government, or art, or commerce, the new ideas, the great steps, have been made by individuals of superior quality and genius, who have, as it were, dragged the mass of the nation up one step to a higher level. So it must be in regard to material progress. The position of the nation to-day is due to the efforts of men like Watt and Arkwright, or, in our own time, to the Armstrongs, the Whitworths, the Kelvins, and the Siemenses. These are the men who, by their discoveries, by their remarkable genius, have produced the ideas upon which others have acted, and which have permeated the whole mass of the nation and affected the whole of its proceedings. Therefore what we have to do, and this is our special task and object, is to produce more of these great men" (Mr. Chamberlain, *Times*, January 18, 1901).

I finally come to the political importance of research. A country's research is as important in the long run as its battleships. The most eloquent teaching as to its national value we owe to Mr. Carnegie, for he has given the sum of £2,000,000 to found a system of endowments, his chief purpose being, in his own words, "to secure if possible for the United States of America leadership in the domain of discovery, and the utilisation of new forces for the benefit of man."

Here is a distinct challenge to Britain. Judging by experience in this country, in spite of the magnificent endowment of research by Mond and Lord Iveagh, the only source of possible competition in the British interest is the State, which certainly could not put the 1/800oth part of the accumulated wealth of the country to better use; for without such help both our Universities and our battleships will become of rapidly dwindling importance.

It is on this ground that I have included the importance of endowing research among the chief points to which I have been anxious to draw your attention.

The Need of a Scientific National Council.

In referring to the new struggle for existence among civilised communities I pointed out that the solution of a large number of scientific problems is now daily required for the State service, and that in this and other ways the source and standard of national efficiency have been greatly changed.

Much evidence bearing upon the amount of scientific knowledge required for the proper administration of the public departments, and the amount of scientific work done by and for the nation, was brought before the Royal Commission on Science presided over by the late Duke of Devonshire now more than a quarter of a century ago.

The Commission unanimously recommended that the State should be aided by a scientific council in facing the new problems constantly arising.

But while the home Government has apparently made up its mind to neglect the advice so seriously given, it should be a source of gratification to us all to know that the application of the resources of modern science to the economic, industrial, and agricultural development of India has for many years engaged the earnest attention of the Government of that country. The Famine Commissioners of 1878 laid much stress on the institution of scientific inquiry and experiment designed to lead to the gradual increase of the food supply, and to the greater stability of agricultural outturn, while the experience of recent years has indicated the increasing importance of the study of the economic products and mineral-bearing tracts.

Lord Curzon has recently ordered the heads of the various scientific departments to form a board, which shall meet twice annually, to begin with, to formulate a programme and to review past work. The board is also to act as an advisory committee to the Government (*Nature*, September 4, 1902), providing among other matters for the proper co-ordination of all matters of scientific inquiry affecting India's welfare.

Lord Curzon is to be warmly congratulated upon the step he has taken, which is certain to bring benefit to our great Dependency.

The importance of such a board is many times greater at home, with so many external as well as internal interests to look after—problems common to peace and war, problems requiring the help of the economic as well as of the physical sciences.

It may be asked, What is done in Germany, where science is fostered and utilised far more than here?

The answer is, There is such a council. I fancy, very much like what our Privy Council once was. It consists of representatives of the Ministry, the Universities, the industries, and agriculture. It is small, consisting of about a dozen members, consultative, and it reports direct to the Emperor. It does for industrial war what military and so-called defence councils do for national armaments; it considers everything relating to the use of brain-power in peace—from alterations in school regulations and the organisation of the Universities, to railway rates and fiscal schemes, including the adjustment of duties. I am informed that what this council advises, generally becomes law.

It should be pretty obvious that a nation so provided must have enormous chances in its favour. It is a question of drilled battalions against an undisciplined army, of the use of the scientific spirit as opposed to the hope of "muddling through."

Mr. Haldane has recently reminded us that "the weapons which science places in the hands of those who engage in great rivalries of commerce leave those who are without them, however brave, as badly off as were the dervishes of Omdurman against the maxims of Lord Kitchener."

Without such a machinery as this, how can our Ministers and our rulers be kept completely informed on a thousand things of vital importance? Why should our position and requirements as an industrial and thinking nation receive less attention from the authorities than the headdress of the Guards? How, in the words of Lord Curzon (*Times*, September 30, 1902), can "the life and vigour of a nation be summed up before the world in the person of its sovereign" if the national organisation is so defective that it has no means of keeping the head of the State informed on things touching the most vital and lasting interests of the country? We seem to be still in the Palæolithic Age in such matters, the chief difference being that the sword has replaced the flint implement.

Some may say that it is contrary to our habit to expect the Government to interest itself too much or to spend money on matters relating to peace; that war dangers are the only ones to be met or to be studied.

But this view leaves science and the progress of science out of the question. Every scientific advance is now, and will in the future be more and more, applied to war. It is no longer a question of an armed force with scientific corps; it is a question of an armed force scientific from top to bottom. Thank God the Navy has already found this out. Science will ultimately rule all the operations both of peace and war, and therefore the industrial and the fighting population must both have a large common ground of education. Already it is not looking too far ahead to see that in a perfect State there will be a double use of each citizen—a peace use and a war use; and the more science advances, the more the old difference between the peaceful citizen and the man at arms will disappear. The barrack, if it still exists, and the workshop will be assimilated; the land unit, like the battleship, will become a school of applied science, self-contained, in which the officers will be the efficient teachers.

I do not thing it is yet recognised how much the problem of national defence has thus become associated with that with which we are now chiefly concerned.

These, then, are some of the reasons which compel me to point out that a scientific council, which might be a scientific committee of the Privy Council, in dealing primarily with the national needs in times of peace, would be a source of strength to the nation.

To sum up, then. My earnest appeal to you is to gird up your loins and see to it that the science of the British Empire shall no longer remain unorganised. I have endeavoured to point out to you how the nation at present suffers from the absence of a powerful, continuous, reasoned expression of scientific opinion, urging in season and out of season that we shall be armed as other nations are, with efficient Universities and facilities for research to uphold the flag of Britain in the domain of learning and discovery, and what they alone can bring.

I have also endeavoured to show how, when this is done, the nation will still be less strong than it need be if there be not added to our many existing councils another, to secure that even during peace the benefits which a proper co-ordination of scientific effort in the nation's interest can bring shall not be neglected as they are at present.

Lest some of you may think that the scientific organisation which I trust you will determine to found would risk success in working on such large lines, let me remind you that in 1859, when the late Prince Consort occupied this Chair, he referred to "impediments" to scientific progress, and said, "they are often such as can only be successfully dealt with by the powerful arm of the State or the long purse of the nation."

If the Prince Consort had lived to continue his advocacy of science, our position to-day would have been very different. His early death was as bad for Britain as the loss of a great campaign. If we cannot make up what we have lost, matters cannot mend.

I have done what I feel to be my duty in bringing the present condition of things before you. It is now your duty, if you agree with me, to see that it be put right. You can if you will.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

SOUTHPORT, 1903.

By Professor W. N. HARTLEY, D.Sc., F.R.S., F.R.S.E., President of the Section.

THE ofttimes laborious method of investigating the relationship of substances by ascertaining how one form of matter can operate upon another—in other words, by chemical reactions—has of late years been supplemented by the examination of their physical properties, and has been extended to compounds, both organic and inorganic. In several directions this has led to results of very uncommon interest. Accordingly I propose to offer a brief account of twenty-five years' experimental work in that branch of chemical physics which deals with the emission and absorption of rays of measurable wave-length, and to review its present position chiefly in relation to the theory of chemistry, indicating where it may be usefully and profitably extended.

According to Davy ("Chemical Philosophy," 1812, vol. i., p. 211), Ritter observed chemical action on moist chloride of silver to be different in different parts of the spectrum, slight in the red, greater towards the violet, and extending into a space beyond the violet where there is no sensible light or heat. Wollaston discovered that chemical action was exerted by refracted rays in a region where they were of a higher refrangibility than any rays that were visible. Young showed that the invisible rays are liable to the same affections as visible rays. Hence we have the beginnings of spectrum analysis in its chemical relations to terrestrial matter, in the infra-red, the visible, and the ultra-violet regions.

Everyone is more or less familiar with the subject of spectrum analysis. This was defined by Tait as an optical method of making a diagnosis of the chemical composition of either (*a*) a self-luminous body, or (*b*) an absorbing medium, whether self-luminous or not. It has now become necessary to enlarge this definition, and I would suggest that it is the study of the composition and the constitution of matter by means of radiant energy, and recording in the order of their refrangibilities the rays emitted and absorbed by matter. By this modified statement the infra red or so-called "invisible heat rays," the visible or "colour rays," and the ultra-violet or "chemical rays" are included.

Spectra are of two kinds, emission and absorption spectra. It will be convenient if the latter are considered first.

ABSORPTION SPECTRA.

The Infra-red Region.

Abney (1880) by the preparation of a particularly sensitive form of collodion emulsion containing silver bromide was successful in obtaining very extraordinary results. Such films as he prepared were so sensitive to invisible radiations of long wave-length as to be capable of forming a representation of even a kettle of boiling water standing in an absolutely dark room. This picture could not of course be properly referred to as a photograph,

though the process by which it was obtained was such as we are accustomed to term a photographic process. It may with greater propriety be termed an actinograph, the result not of light, but of dark rays. The least refrangible of the visible rays lies about wave-length 7800 ten-millionths of a millimetre, or Angström units; but these rays extend as far as wave-length 12,000, while Becquerel has measured lines in the spectra of metals of as low a refrangibility as wave-length 18,000.

Abney and Festing (1881) investigated the influence of atomic groupings in the molecules of organic substances by measuring their absorption in the infra-red region of the spectrum.

They studied such simply constituted substances as water, hydrochloric acid, chloroform, carbon tetrachloride, and cyanogen, besides many hydrocarbons with their hydroxyl, haloid, and carboxyl derivatives. Characteristic groups of lines or very narrow bands were observed in carbon compounds, but they are absent from carbon compounds, containing no hydrogen, and do not all appear in some of the hydrogen compounds. The facts observed led to the conclusion that they belonged to hydrogen, but are subject to some occasional modifications. Oxygen in hydroxyl, for instance, modifies two of the lines, since it obliterates by absorption the rays which lie between them. Oxygen in aldehyde, or when it forms part of the carbon nucleus of some such compound, presents bands which are bounded by well-defined lines, or are inclined to be linear. These appear to be characteristic bands indicating the carbon nucleus of a series of substances. Alkyl radicals, such as ethyl, exhibit absorption bands, and so does the benzene nucleus. It is a remarkable fact that bands appear in the solar spectrum which correspond with those of benzene (1881).

Julius (1893) has investigated the absorption in the infra-red caused by many carbon compounds by means of the bolometer, combined with a prism, and also with a diffraction grating. He showed that the molecules of compound substances absorbed the rays which were emitted at the time of their formation. Thus, to take the simplest case, the emission spectrum of hydrogen burning in air corresponds with the absorption bands of water vapour; that is to say, the absorption spectra of the compounds are the counterpart of the emission spectra of the flames which yield these compounds during combustion. The emission spectrum of carbon dioxide is found in the spectrum of burning carbon monoxide, cyanogen, methane, and carbon disulphide; and that of water vapour in various hydrocarbons. As early as 1888 Julius, in an Inaugural Dissertation, quoting Tyndall, recognised that the absorption and emission of rays measured with the thermopile were manifestations of the molecular vibrations.

The various absorption spectra examined included those of the alcohols, such as isopentylic, isobutylic, normal butylic, propylic, ethylic, and methylic, as well as hydrocarbons, chloroform, and benzene. The study of the maxima of radiation and the maxima of absorption offers us a means of arriving at a knowledge of a series of new and valuable physical constants, namely, the vibration periods characteristic of the molecules. (Tyndall discussed this subject in his usually luminous style on pages 391 to 402 of his work "Heat as a Mode of Motion").

Puccianti (1900) has examined the infra-red absorption spectra of liquids, including aromatic compounds and alkyl derivatives, while Donath has examined in the same region various essential oils. Carbon combined with hydrogen shows a maximum of absorption with a wave-length about (1·71 μ m.m.) 17,100 Angström units.

Benzene and pyridine have two other maxima of absorption in common. The alcohols have very similar maxima of absorption at wave-length 21,000.

The three isomeric xylenes show absorption spectra which are almost identical. At or about wave-length 23,200 another maximum of absorption is shown.

Julius refers to Langley's observation that at a wave-length of 27,000 there is an abrupt termination to the solar spectrum, probably caused by the water vapour in the atmosphere; but a band extends to 273,000, and at no very great elevation above the earth's surface there are rays with a wave-length of 45,700 Angstrom units. All radiations of longer wave-length—and Julius has measured down to 149,000 Angström units—are likely to be absorbed by the carbon dioxide in the atmosphere.

The Visible Rays or Colour Region.

J. L. Schönn (1879) examined the absorption spectra of substances usually considered to be colourless in layers from 1·6 to 3·7 metres in thickness and observed narrow bands in the spectra of methyl, ethyl, and amyl alcohol, lying in the red, orange, and yellow; methyl alcohol showed two bands, ethyl and amyl alcohol each three. Gerard Krüss (1888) calculated the wave-lengths of these bands, and it appears that the higher members of the homologous series have the bands displaced towards the red end of the spectrum. Russell and Lapraik (1879) made similar observations on columns of liquid from two to eight feet in length. All the substances gave well-defined absorption bands lying between wave-lengths 6000 and 7000.

The bands of the different substances differed altogether from the bands of water. Alcohols give a band which is similar in different alcohols, but the higher the alcohol stands in the homologous series—that is to say, the larger the number of carbon atoms it contains—the nearer is the band to the red end of the spectrum (1881).

It was definitely established that for each CH_3 introduced into a molecule of ammonia or benzene there is a shifting of the absorption bands towards the red end o the spectrum.

It will, of course, be understood that the liquids examined were perfectly colourless in the ordinary acceptation of the term; and that they appear so is owing to the bands of absorption being very narrow, so that the percentage of luminous rays withdrawn by absorption is but a very small fraction of the whole spectrum emitted by a source of light when viewed under ordinary conditions.

Numerous observations were made by Melde, Burger, Magnus, H. W. Vogel, and Landauer (1876-78), which showed that changes in the absorption spectra of solutions are partly physical and partly chemical; that is to say, they are caused by changes in the constitution of the solution. Vogel mentions cases where no chemical change was believed to take place, as, for instance, where naphthalene red shows different spectra according to whether it is dissolved in alcohol, water, resin, or is solid or used to colour paper (1878).

This points to some difference in the constitution of the solution. A well-known instance is that of iodine in alcohol, chloroform, or carbon disulphide.

It must be observed that Vogel's work referred merely to phenomena observable in the visible spectrum, to small thicknesses of the absorbing medium, and was not applied quantitatively. Two solutions may give spectra which are apparently identical at one concentration, but spectra quite different when submitted to varying degrees of dilution.

In order to ascertain in what way absorption spectra are related to the chemical constitution of organic substances, it is necessary to examine a wider range of spectrum than that included in the merely visible region, and this may be done by extending the observations into the ultra-violet.

The Ultra-violet Region.

Stokes in preparing his experiments for a Friday evening discourse at the Royal Institution observed that the spectrum of electric light when a prism and lenses of quartz were used extended no less than six or eight times the length of the visible spectrum. In 1862 he studied the ultra-violet spectra of metals and executed drawings of the lines exhibited by aluminium, zinc, and cadmium. He discovered the fact that certain solutions show light and dark bands in the spectrum of rays transmitted by them, the solutions being colourless; the bands are invisible

unless they fall on a fluorescent screen. It was under such conditions that they exhibited light and darkness. The screen used was of plaster-of-Paris saturated with a fluorescent substance, such as uranium phosphate.

William Allen Miller in 1863, simultaneously with Stokes, described his method of examining the photographic transparency of various saline solutions and organic substances and of depicting metallic spectra. A sensitised photographic plate was used for the reception of the rays of the spectrum, so that they were made to register their own position and intensity. L. Soret invented the fluorescent eye-piece for the purpose of investigating the ultra-violet rays, and ascertained the best media for the transmission of rays of high refrangibility. Colourless fluor-spar, a rare mineral, was found to answer best, and quartz lenses were achromatised with this. Iceland spar was found to absorb some of the more refrangible rays, and a pure spectrum was difficult to obtain with quartz prisms owing to double refraction, which caused the lines in metallic spectra to be duplicated. Struck by the fact that Miller had examined many organic substances without obtaining evidence of a connection between their constitution and their absorption spectra—the actual words used by Miller were, "I have not been able to trace any special connection between the chemical complexity of a substance and its diactinic power" (*Journ. Chem. Soc.*, vol. xi., p. 68)—it appeared to me desirable that this point should be systematically re-investigated. L. Soret had already proceeded with work in this direction, by examining and drawing a great variety of organic substances and diagrams of absorption curves. But it was deemed necessary to make a large number of examinations of substances of a comparatively simple constitution, and according to theory closely related, and afterwards gradually to proceed to the study of substances of greater complexity. For such purposes a photographic method alone appeared a practicable one, particularly when comparisons had to be made between substances observed at different times, for the reason that none but photographic records could be absolutely relied upon and stored away for future reference.*

The plan of the proposed investigation was to photograph the rays transmitted by molecular proportions of hydrocarbons, alcohols, acids, and esters, either alone as vapour or liquid, or dissolved in some neutral and, in comparison with the substances to be examined, an optically non-absorbent solvent.

It was considered that the metameric esters would afford much information if a sufficient number of them were examined and their spectra compared, and if the acids themselves were not responsive the sodium and potassium salts in solution would serve the purpose, since the alkalis did not affect the spectrum. The general deductions (1879) are now well known, but two points not generally taken into account were well established. First, the extraordinary delicacy of the ultra-violet spectrum in detecting traces of impurities. For instance, pyridine, an invariable impurity in commercial ammonia, is present in the proportion of about $\frac{1}{30000}$th. It was proved that the absorption spectra of the normal paraffins, prepared with the greatest care by Schorlemmer, contained traces of impurities which could not be separated. Secondly, some of the normal alcohols could not be rendered pure by the ordinary methods employed, and great care was necessary in their preparation. It may well be asked that, if such were the case, upon what grounds was it concluded that impurities were present? How was it possible to distinguish between a normal and an abnormal absorption spectrum when no standards of comparison existed? It may be of interest if this question be now answered, as no adequate account of it has been made public. All the substances in any one homologous series were shown to vary in the extent to which the rays at the more refrangible end of the spectrum were absorbed, and the different terms of the series differ solely by the number of CH_2 groups in the molecule; and the greater the number of these the greater the absorption. The extent of the absorption should be proportional to the molecular weight of the substance. Accordingly, if repeatedly purifying and fractionally distilling a considerable quantity of material failed to give spectra which were constant and identical, but gave instead spectra which were variable, even in a slight degree, it was evident that the absorption due to the molecule of the substance was interfered with by some impurity.

When, however, it became evident that successive quantities of methylic alcohol, for example, prepared in a certain manner yielded spectra which were practically identical under different conditions, such as thickness of liquid, and that they differed but slightly from that of pure water after the type of which the alcohol is constituted, the conclusion was inevitable that we were dealing with a pure preparation. In short, the longest spectrum obtained under all circumstances and under every reasonable condition could not possibly be the result of accident, more particularly if it could be repeatedly obtained from different specimens of the same substance. The same reasoning applies to the acids and their salts in the investigation of which similar difficulties arose.

Soret and Rilliet pointed out that in the rectification and prolonged desiccation of the alcohols there is often slight oxidation which leads to the production of impurities which affect the spectra transmitted by them.

They found that ethyl alcohol is not appreciably less diactinic than methyl alcohol, and both transmitted a spectrum nearly as long as that of water. This was shown by Huntington and me when the usual 25 m.m. of thickness of the layer of liquid were tested. By taking columns of liquid 100 m.m. in length the differences are greater, and they increase with columns of increased length.

The influence of each additional CH_2 in the molecule causes a shortening of the spectrum. This was shown to be due to the carbon atoms and not to the hydrogen. The acids, containing the same number of carbon atoms as the alcohols, have a much greater absorptive power, which is due to the carboxyl group (C:O·OH). By the examination of a number of various substances, such as polyhydric alcohols, as glycol, glycerol, mannitol, and various sugars, it was found that, no matter what its complexity, no open-chain compound causes selective absorption, *i.e.*, absorption bands.

Shortly it may be stated that in the examination of organic substances we have three variations in absorption spectra:—First, those of substances the rays of which are freely transmitted, the absorption being at the more refrangible end of the spectrum, and the spectrum of which is readily increased in length by dilution; secondly, those

* Clerk Maxwell had calculated for Miller the best focal length of lenses of quartz which would give an approximately flat field. His computation made this something over a length of three feet. All Miller's photographs were taken with the plate placed normal to the axis of the lens, but Stokes had shown that the locus of the foci of the different rays formed an arc of a curve or nearly a straight line, lying very obliquely to the axes of the pencils coming through the lens.

It was obvious from Miller's photographs that only one or two rays on each plate were even approximately in focus. To obtain spectra in focus from end to end it was evidently necessary to incline the plate so that the end upon which the red rays would fall, which are of longest wave-length, should be farther off than that upon which the ultra-violet fall, which are of shortest wave-length. It was also found experimentally that lenses of much shorter focal length (10 or 12 inches) could be used, giving perfect definition, and, what is still more important, it was found a positive advantage not to have them corrected by fluor-spar or calcite. The plate carrier was adjusted at an inclination of approximately 22° to the normal; in such a position the rays from the yellow sodium line to the extreme ultra-violet of the spark spectrum of cadmium were simultaneously in focus on a plane surface.

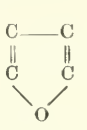
The prism was of quartz cut on Cornu's plan, the method of construction designed to get rid of all double refraction being communicated to me by M. Cornu in a very kindly written letter. The first instrument was constructed in 1878 and the description of it published in 1881. It has been the model for several others. One with two prisms and lenses of 12 inches focus was exhibited by me in the Inventions Exhibition in 1882. At the Jubilee Meeting of the British Association at York the spark spectra of iron, cobalt, and nickel, enlarged to twenty-five diameters and printed by the Autotype Company, were exhibited. They are over 8 feet in length, and have proved very useful for reference. The photographic process is a point of great importance; the then newly invented gelatin bromide films made by Kennet were alone quite suitable

in which the spectra are of the same kind, but the absorptive power is greater, so that they withstand dilution to a much greater extent; thirdly, those spectra which exhibit selective absorption, and which at the same time exert great absorptive power, or, in other words, can undergo great dilution before the absorption bands are rendered visible, and still further dilution before they are extinguished or obliterated.

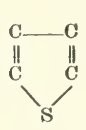
Spectra of the First Variety belong to substances which are constructed on an open chain of carbon atoms, thus :— C·C·C·C·C or C=C·C·C·C and C≡C·C·C·C.

The introduction in place of one or more atoms of hydrogen—of hydroxyl, OH, carboxyl, COOH, methoxyl, OCH_3, CO, COH, or NH_2, or of side chains such as CH_3, C_2H_5, &c.—does not affect the character of the spectra, but merely the absorptive power, which is increased when oxygen or an oxygenated radical is introduced.

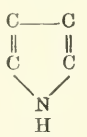
Spectra of the Second Variety are spectra of substances so constituted that the carbon atoms form a closed chain. It is immaterial whether the closed chains are homocyclic or heterocyclic; thus :—



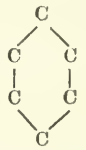
Furfurane.



Thiophene.

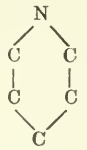


Pyrrol.



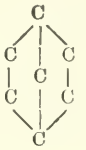
Diketohexamethylene

Hydro-aromatic compounds.

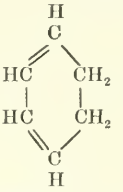


Piperidine.

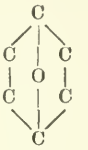
Cyanuric Acid.



Camphor.



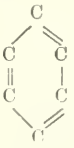
Dihydrobenzene.



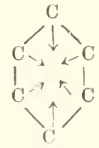
Cineol.

They possess greater absorptive power than open-chain compounds, but do not exhibit absorption bands. It is manifestly the chain or ring structure of the compounds that gives them greater absorptive power, and not the number of carbon atoms in the molecules.

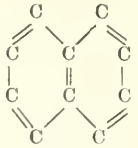
Spectra of the Third Variety.—These show absorption bands, and the substances yielding them are generally constituted on the type of benzene, naphthalene, anthracene, phenanthrane, &c.; but the rings may be either homocyclic or heterocyclic without the character of the spectra being altered; thus :—



Benzene.

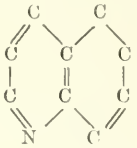


Benzene.

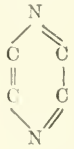


Naphthalene.

Pyridine.



Quinoline.



Pyrazine.

If we say that the compounds which are homocyclic are constituted of at least three pairs of carbon atoms doubly linked, which are themselves singly linked together, we may make use of the formula of Kekulé for benzene as the simplest expression of their constitution; if we assume that each of the six atoms is linked to at least other two atoms we adopt what is practically the prism formula of Ladenburg, or the same idea expressed in space of two dimensions. It is difficult to express the physical condition by the Armstrong-Baeyer formula or centric arrangement because this does not clearly suggest to one's mind what is manifestly the fact, namely, that the carbon atoms in the nucleus of benzene are much more closely condensed or combined together than those of the hydroaromatic series. This condensed condition of the carbon atoms is evident from the higher molecular refractive energy of aromatic compounds and of the specific refractive energy of the carbon in such combinations.

Side chains such as do not exert selective absorption have no influence on the character of the spectra, but they slightly increase the general absorption.

Heterocyclic compounds possess greater absorptive power, both as regards the general and selective absorption, than those which are homocyclic.

The point which I particularly desire to draw attention to here is, that for the first time Kekulé's remarkable benzene theory was supported by definite physical measurements, and the closed-ring formula represented a veritable actuality.

Of Molecular and Intra-molecular Vibrations.

Johnstone Stoney was the first to show that the cause of the interrupted spectra of gases is to be referred to the motions within the individual molecules and not to the irregular journeys or encounters of the molecules with each other; and this applies to the absorption as well as to emission spectra. He further advised the use of oscillation frequencies instead of wave-lengths in describing the measurements of spectra. Johnstone Stoney and Emerson Reynolds subsequently examined the extraordinary absorption exhibited by chlorochromic anhydride, the bands in which are evidently harmonically related.

It has already been shown that the hydrocarbons of the aromatic series exert two kinds of absorption, a general and a selective absorption. All the evidence we possess warrants the belief that the general absorption is caused by the motion of the molecules, while the selective absorption is due to the motion within the molecules.

When the molecule of a substance is capable of vibrating synchronously with a radiation, the ray received on this substance is absorbed. The absorption is complete if the direction of the vibration of the molecule and of the ray is the same but the phase opposite, and if the number of molecules in the path of the rays is sufficient to damp all the vibrations.

When the quantity of substance in the path of the rays is reduced, the number of molecules present is not sufficient to damp all the vibrations, and some of the rays are trans-

mitted. If, however, certain carbon atoms within the molecule are vibrating synchronously with certain rays, we shall have selective absorption of these rays after the general absorption has been so weakened by dilution or otherwise as to allow them to pass.

It is evident, then, that general selective absorption exerted by carbon compounds is due to the vibration of the molecules because the absorption increases with the number of carbon atoms in the molecule; or, in other words, in any homologous series the greater the molecular mass the lower the rate of vibration of the molecule.

It has not been found possible to associate any of the absorption bands of the substances examined with any particular carbon atoms; but the bands in benzene are six in number, or the same in number as the carbon atoms. It has, however, been shown that the rapidity of the intra-molecular vibrations was dependent upon the rate of vibration of the molecules. From numbers representing approximately the mean wave-lengths of the four chief bands of rays absorbed by benzene, naphthalene, and anthracene, and from the velocity of light, the mean rate of the vibrations within the molecules was calculated (1881), the numbers being as follows:—

	Molecular vibrations.
Benzene	1248^{10}
Naphthalene	1177^{10}
Anthracene	910^{10}

The mean rate of vibration of the rays absorbed by naphthalene is less than that absorbed by benzene, and those of anthracene less than those of naphthalene. It follows from this that the vibrations within the molecules are not independent, but are a consequence, of the fundamental molecular vibrations, like the harmonics of a stretched string or of a bell.

The term absorptive power has generally been used with respect to the extent of rays of the spectrum absorbed, but there is intensity of absorption to be considered. In the case of a vibrating string or tuning-fork greater amplitude of vibration means a louder note; in the case of molecules greater intensity of absorption may be caused by a greater amplitude of vibration in the molecules of the absorbing medium, the number of molecules being constant. But by greater amplitude it is not to be understood that the rate of vibration is increased.

If this be so then, as the absorption intensity of anthracene and naphthalene is, molecule for molecule, greater than that of benzene, the amplitude of vibration of the molecules of these substances is greater, but the rate of vibration is slower.

From the foregoing it will be observed that where λ is the wave-length $\frac{1}{\lambda}$ is the inverse wave-length, and, omitting the correction for the refraction of air, which is a very small value, it is the oscillation frequency of the ether in a small unit of time, and the most convenient measurement for use in describing spectra. Seven years after the publication of these views, Gerard Krüss (1888) dealt with the subject of coloured substances in a similar manner. From the undulatory theory of light, deductions may be drawn regarding the inner molecular movements or inter-atomic movements within the molecules, inasmuch as the vibrations of the ether, which fills the intra-molecular space, are a resultant within that space of the velocity and ampli ude of the molecular vibrations.

Thus, if λ be the wave-length of a ray emitted by a substance, and v the velocity of light, the number of vibrations, n, which a molecule sends forth by movements of it as a whole and of its parts can be determined by the equation

$$n = \frac{v}{\lambda}.$$

G. Krüss made a series of calculations for coloured substances similar to those which I had made for colourless substances and for ozone.

Curves of Molecular Vibrations.

Observations on absorption spectra should, whenever it is possible, be made with reference to the quantity of substance which produces a given measurable effect. A molecular weight in milligrms. or a milligrm.-molecule is a convenient quantity which may be dissolved in 20 c.c., 40 c.c., or 100 c.c. of any non-absorbent liquid, and observed through thicknesses of the solution varying from 25 m.m. to 1 m.m. in thickness. When a series of photographs have been measured a curve is plotted, which shows the general and the selective absorption of the substance. The oscillation frequencies of the absorbed rays are taken as abscissæ, and the proportional thickness in millimetres of the weakest of a series of solutions as ordinates. The curves are as often as possible made continuous, and they are called *curves of molecular vibrations*.

The curves of the molecular vibrations present very striking features: they are valuable physical constants which enable one to classify and identify substances.

Position Isomerism.

Isomerides of the *ortho*-, *meta*-, and *para*-positions in aromatic substances yield spectra with the absorption bands, differing in position, in width, and in intensity, There is no distinguishing character to be observed in the different isomerides. Isomerism in the pyridine, quinoline, and naphthalene derivative has not yet been completely studied. In such cases as have already passed under review there is nothing that indicates the positions of the substituted hydrogens.

Stereo-isomerism.

Where isomerism is not due to differences in structure, but simply to the distribution of the atoms in space, we have no means of distinguishing isomeric substances from an examination of their spectra; for instance, benz-*syn*-aldoxime and benz-*anti*-aldoxime yield curves of molecular vibrations which are identical.

(To be continued).

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 135).

Chapter II. (*continued*).

Polonium.

As I said above, by passing sulphuretted hydrogen through the various hydrochloric acid solutions obtained during the course of the process, active sulphides are precipitated, of which the activity is due to polonium. These sulphides chiefly contain bismuth, a little copper and lead; the latter metal occurs in relatively small amount, because it has been to a great extent removed by the soda solution, and because its chloride is only slightly soluble. Antimony and arsenic are found among the oxides only in the minutest quantity, their oxides having been dissolved by the soda. In order to obtain the very active sulphides, the following process was employed:—The solutions made strongly acid with hydrochloric acid were precipitated with sulphuretted hydrogen; the sulphides thus precipitated are very active, and are employed for the preparation of polonium; there remain in the solution substances not completely precipitated in presence of excess of hydrochloric acid (bismuth, lead, antimony). To complete the precipitation, the solution is diluted with water, and treated again with sulphuretted hydrogen, which gives a second precipitate of sulphides, much less active than the first, and which have generally been rejected. For the further purification of the sulphides, they are washed with ammonium sulphide, which removes the last remaining

* Thesis presented to the Faculté des Sciences de Paris.

traces of antimony and arsenic. They are then washed with water and ammonium nitrate, and treated with dilute nitric acid. Complete solution never occurs; there is always an insoluble residue, more or less considerable, which can be treated afresh if it is judged expedient. The solution is reduced to a small volume and precipitated either by ammonia or by excess of water. In both cases the lead and the copper remain in solution; in the second case, a little bismuth, scarcely active at all, remains also in solution.

The precipitate of oxides or basic nitrates is subjected to fractionation in the following manner:—The precipitate is dissolved in nitric acid, and water is added to the solution until a sufficient quantity of precipitate is formed; it must be borne in mind that sometimes the precipitate does not at once appear. The precipitate is separated from the supernatant liquid, and re-dissolved in nitric acid, after which both the liquids thus obtained are re-precipitated with water, and treated as before. The different fractions are combined according to their activity, and concentration is carried out as far as possible. In this way is obtained a very small quantity of a substance of which the activity is very high, but which, nevertheless, has so far only shown bismuth lines in the spectroscope.

There is, unfortunately, little chance of obtaining the isolation of polonium by this means. The method of fractionation just described presents many difficulties, and the case is similar with other wet processes of fractionation. Whatever be the method employed, compounds are readily formed which are absolutely insoluble in dilute or concentrated acids. These compounds can only be re-dissolved by reducing them to the metallic state, *e.g.*, by fusion with potassium cyanide. Considering the number of operations necessary, this circumstance, constitutes an enormous difficulty in the progress of the fractionation. This obstacle is the greater because polonium, once extracted from the pitchblende, diminishes in activity. This diminution of activity is slow, for a specimen of bismuth nitrate containing polonium only lost half its activity in eleven months.

No such difficulty occurs with radium. The radio-activity remains throughout an accurate gauge of the concentration; the concentration itself presents no difficulty, and the progress of the work from the start can be constantly checked by spectral analysis.

When the phenomena of induced radio-activity, which will be discussed later on, were made known, it seemed obvious that polonium, which only shows the bismuth lines and whose activity diminishes with time, was not a new element, but bismuth made active by the vicinity of radium in the pitchblende. I am not sure that this opinion is correct. In the course of my prolonged work on polonium, I have noted chemical effects, which I have never observed either with ordinary bismuth or with bismuth made active by radium. These chemical effects are, in the first place, the extremely ready formation of insoluble compounds of which I have spoken above (especially basic nitrates), and, in the second place, the colour and appearance of the precipitates obtained by adding water to the nitric acid solution of bismuth containing polonium. These precipitates are sometimes white, but more generally of a more or less vivid yellow, verging on red.

The absence of lines other than those of bismuth does not necessarily prove that the substance only contains bismuth, because bodies exist whose spectrum reaction is scarcely visible.

It would be necessary to prepare a small quantity of bismuth containing polonium in as concentrated a condition as possible, and to examine it chemically, in the first place determining the atomic weight of the metal. It has not yet been possible to carry out this research on account of the difficulties of a chemical nature already mentioned.

If polonium were proved to be a new element, it would be no less true that it cannot exist indefinitely in a strongly radio-active condition, at least when extracted from the ore. There are therefore two aspects of the question:—First, whether the activity of polonium is entirely induced by the proximity of substances themselves radio-active, in which case polonium would possess the faculty of acquiring atomic activity permanently, a faculty which does not appear to belong to any substance whatever; second, whether the activity of polonium is an inherent property, which is spontaneously destroyed under certain conditions, and persists under certain other conditions, such as those which exist in the ore. The phenomenon of atomic activity induced by contact is still so little understood, that we lack the ground on which to formulate any opinion on the matter.

(Note.—A work has recently appeared on polonium by M. Marckwald. He plunges a small rod of pure bismuth into a hydrochloric acid solution of the bismuth extracted from the pitchblende residue. After some time the rod becomes coated with a very active deposit, and the solution now contains only inactive bismuth. M. Marckwald also obtains a very active deposit by adding tin chloride to a hydrochloric acid solution of radio-active bismuth. From this he concludes that the active element is allied to tellurium, and gives it the name of *radiotellurium*. This active substance of M. Marckwald seems identical with polonium, from its behaviour, and from the easily absorbed rays it emits. The choice of a new name for this substance is futile in the present state of the question).

Preparation of the Pure Chloride of Radium.

The method by which I extracted pure radium chloride from barium chloride containing radium consists in first subjecting the mixture of the chlorides to fractional crystallisation in pure water, then in water to which hydrochloric acid has been added. The difference in solubility of the two chlorides is thus made use of, that of radium being less soluble than that of barium.

At the beginning of the fractionation, pure distilled water is used. The chloride is dissolved, and the solution raised to boiling-point, and allowed to crystallise by cooling in a covered capsule. Beautiful crystals form at the bottom, and the supernatant, saturated solution is easily decanted. If part of this solution be evaporated to dryness, the chloride obtained is found to be about five times less active than that which has crystallised out. The chloride is thus divided into two portions, A and B—portion A being more active than portion B. The operation is now repeated with each of the chlorides A and B, and in each case two new portions are obtained. When the crystallisation is finished, the less active fraction of chloride A is added to the more active fraction of chloride B, these two having approximately the same activity. Thus there are now three portions to undergo afresh the same treatment.

The number of portions is not allowed to increase indefinitely. The activity of the most soluble portion diminishes as the number increases. When its activity becomes inconsiderable, it is withdrawn from the fractionation. When the desired number of fractions has been obtained, fractionation of the least soluble portion is stopped (the richest in radium), and it is withdrawn from the remainder.

A fixed number of fractions is used in the process. After each series of operations, the saturated solution arising from one fraction is added to the crystals arising from the following fraction; but if after one of the series the most soluble fraction has been withdrawn, then, after the following series, a new fraction is made from the most soluble portion, and the crystals of the most active portion are withdrawn. By the successive alternation of these two processes, an extremely regular system of fractionation is obtained, in which the number of fractions and the activity of each remains constant, each being about five times as active as the subsequent one, and in which, on the one hand, an almost inactive product is removed, whilst, on the other, is obtained a chloride rich in radium. The amount of material contained in these fractions gradually diminishes, becoming less as the activity increases.

At first six fractions were used, and the activity of the chloride obtained at the end was only o·1 that of uranium.

When most of the inactive matter has been removed, and the fractions have become small, one fraction is removed from the one end, and another is added to the other end consisting of the active chloride previously removed. A chloride richer in radium than the preceding is thus obtained. This system is continued until the crystals obtained are pure radium chloride. If the fractionation has been thoroughly carried out, scarcely any trace of the intermediate products remain.

At an advanced stage of the fractionation, when the quantity of material in each fraction is small, the separation by crystallisation is less efficacious, the cooling being too rapid and the volume of the solution to be decanted too small. It is then advisable to add water containing a known quantity of hydrochloric acid; this quantity may be increased as the fractionation proceeds.

The advantage gained thus consists in increasing the quantity of the solution, the solubility of the chlorides being less in water acidified with hydrochloric acid than in pure water. By using water containing much acid, excellent separations are effected, and it is only necessary to work with three or four fractions.

The crystals, which form in very acid solution, are elongated needles, those of barium chloride having exactly the same appearance as those of radium chloride. Both show double refraction. Crystals of barium chloride containing radium are colourless, but when the proportion of radium becomes greater, they have a yellow colouration after some hours, verging on orange, and sometimes a beautiful pink. This colour disappears in solution. Crystals of pure radium chloride are not coloured, so that the colouration appears to be due to the mixture of radium and barium. The maximum colouration is obtained for a certain degree of radium present, and this fact serves to check the progress of the fractionation.

I have sometimes noticed the formation of a deposit composed of crystals of which one part remained uncoloured, whilst the other was coloured, and it seems possible that the colourless crystals might be sorted out.

The fractional precipitation of an aqueous solution of barium chloride by alcohol also leads to the isolation of radium chloride, which is the first to precipitate. This method, which I first employed, was finally abandoned for the one just described, which proceeds with more regularity. I have, however, occasionally made use of precipitation by alcohol to purify radium chloride which contains traces of barium chloride. The latter remains in the slightly aqueous alcoholic solution, and can thus be removed.

M. Giesel, who, since the publication of our first researches, has been preparing radio-active bodies, recommends the separation of barium and radium by fractional crystallisation in water from a mixture of the bromides. I can testify that this method is advantageous, especially in the first stages of the fractionation.

(To be continued).

POINTS IN THE SYNTHESIS OF CAMPHOR AND OF INDIARUBBER.

By JOHN GEDDES McINTOSH.

The crude product obtained by the action of hydrochloric acid on American spirits of turpentine, when distilled by my patent process over soda-ley, yields a small quantity of a residual substance which I believe to be identical with Bouchardat's so-called synthetic rubber from isoprene.

When the *solid* pinene mono-hydrochloride is distilled with zinc-dust, it is entirely converted into a *liquid* compound, the properties of which I am investigating. Unlike other distillates obtained by the use of various other reagents, this one is entirely free from chlorine.

Analytical Laboratory,
9, Parsonage Street, Cubitt Town, E.,
September 8, 1903.

CORRESPONDENCE.

RADIUM AND HELIUM.

To the Editor of the Chemical News.

Sir,—It appears from the work of Sir William Ramsay and Mr. Soddy that the radium emanation is actually producing helium (and, presumably, other bodies of the same class), the process being associated with the decay of the radio-activity of the emanation. This fact seems to establish a connection between valency and radio-activity—a view which has been previously expressed in your columns (*vide* Chemical News, 1901, lxxxiii., 130; 1902, lxxxv., 205 and 310). For it certainly looks as if a divalent element like radium, by the simple process of throwing off electrons (or valency bonds, on the Helmholtz theory of valence), is producing bodies of a non-valent nature.—I am, &c.,

Geoffrey Martin.

Kiel, August 30, 1903.

PATENTS FOR INVENTIONS.

To the Editor of the Chemical News.

Sir,—It is probable that the majority of British inventors and patentees are aware of the introduction of an "Australian Federal Patents Bill" by the Commonwealth of Australia.

The Bill was presented and read on the 26th day of June last, and will probably become law in the Commonwealth by the beginning of next year.

The Bill contains one provision of such far-reaching consequence that we think too much prominence cannot be given to it. The provision we refer to is contained in Section 83, as follows:—

"Every patent shall be granted subject to the following conditions:—

(*a*). That the patentee or some person authorised by him shall within five years after the date thereof commence and after such commencement continuously carry on in Australia the construction manufacture or working of the invention patented in such a manner that any person desiring to use it may obtain it or the use of it at a reasonable price; and

(*b*). That the patentee shall not after four years from the date of the patent import the invention or cause it to be imported into Australia."

Thus it follows that an English manufacturer who obtains a patent for his product in the Australian Commonwealth must actually manufacture on the spot, and refrain from exporting the same from this country after a period of four years or lose his patent.

We also beg to draw your attention to the Canadian Patent Law which was amended by the Act of August 13, 1903, and which provides that the patentee or his representative must within two years commence and continuously carry on in Canada the construction or manufacture of his invention.

If, after the expiration of twelve months from the grant of a patent, the patentee or his representative imports into Canada the invention for which the patent is granted the patent shall be void.

These provisions are so widely different from the provisions in the mother country, and are likely to very seriously affect the position of British patentees, that no excuse is necessary for drawing your attention to the same.—We are, &c.,

J. E. Evans-Jackson and Co.

Bristol House,
19 & 20, Holborn Viaduct, London, E.C.,
September 9, 1903.

CHEMICAL NOTICES FROM FOREIGN SOURCES

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 6, August 10, 1903.

Description of a New Apparatus for the Preparation of Pure Gases.—Henri Moissan.—The author describes an apparatus which overcomes a number of the difficulties associated with the preparation of pure gases, and using this prepares pure specimens of carbon dioxide, hydriodic acid, hydrochloric acid, hydrogen phosphide, sulphuretted hydrogen, and nitric oxide.

Certain Binary Compounds of Uranium.—A. Colani.—The author employs the double chloride of uranium and sodium, $UCl_2,NaCl$, for the preparation of various uranium compounds. This substance has the advantage of being very slightly hygroscopic, and is scarcely more volatile than NaCl. He prepares in a pure state and investigates the properties of the sulphide, selenide, and telluride, nitride, phosphide, arsenide, and antimonide of uranium, and finds that the compounds of uranium with the trivalent metalloids burn with difficulty in air, but if thrown into the flame of a Bunsen burner cause brilliant sparks to appear. They are all violently attacked by concentrated nitric acid.

No. 7, August 17, 1903.

Properties of Nickel Steels.—Léon Guillet.—The author devises a diagram showing the properties of nickel steels. It contains four spaces; one corresponding to steels having the same structure as carbon steels, another to martensite with iron, a third to pure martensite, and the fourth to pure iron. The diagram also allows of the composition of the steels being deduced from its structure, and consequently its mechanical properties.

Disymmetric Tetramethyldiamino-Diphenylene-phenylmethane and the Colouring matter which is Derived from it.—A. Guyot and M. Granderye.—To prepare disymmetric tetramethyldiamino-diphenylene-phenylmethane the *o*-amine-derivative of the leucobose green malachite is dissolved in sulphuric acid, and treated with a solution of sodium nitrite, first at a low temperature, and finally at 100° to decompose the diazoic compounds. The yield under these conditions is about 16 per cent of the theoretical yield. The substance is then purified by being several times crystallised by precipitation from benzine by means of boiling alcohol in the form of fine white crystals melting at 149°, very soluble in benzine and very slightly soluble in alcohol.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemistry) at the Southport Meeting of the British Association :—

President—Prof. Walter Noel Hartley, D.Sc., F.R.S., F.R.S.E.

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The Papers brought before the Section were as follows:—

President's Address.

Prof. J. Campbell Brown—Apparatus for determining Latent Heat of Evaporation.

Miss Ida Smedley—On some Derivatives of Fluorene.

A. R. Ling—Action of Diastase on the Starch Granules of Raw and Malted Barley.

A. R. Ling—Action of Malt Diastase on Potato Starch Paste.

B. F. Davis and *A. R. Ling*—Action of Malt Diastase on Potato Starch Paste.

Dr. H. C. White—The Chemical and Physical Characteristics of the so-called Mad-stone.

Prof. E. A. Letts, R. F. Blake, and *J. S. Totton*—Reduction of Nitrates by Sewage.

R. L. Taylor—A Method for the Separation of Cobalt from Nickel, and the Volumetric Determination of Cobalt.

Dr. H. E. Armstrong—Report of Committee on Isomorphous Sulphonic Derivatives of Benzene.

Dr. H. E. Armstrong—Report of Committee on Isomeric Naphthalene Derivatives.

Dr. M. O. Forster—Report of Committee on the Possibility of making Special Reports more Available than at Present.

Sir Henry E. Roscoe—Report of the Committee on Duty Free Alcohol.

J. Hübner and *Prof. W. J. Pope*—The cause of the Lustre produced on Mercerising Cotton under Tension.

Prof. James Dewar—Investigations at Low Temperatures: —(*a*) Densities of Solid Hydrogen, Nitrogen, and Oxygen. (*b*) Methods of Producing Solid Hydrogen and Nitrogen. (*c*) Latent Heat, Specific Heat, and Coefficient of Expansion of Liquid Hydrogen.

Dr. A. Macfadyen—The Application of Low Temperatures to the Study of Biological Problems.

Prof. T. Turner—Stead's Recent Experiments on the Causes and Prevention of Brittleness in Steel.

W. Ackroyd—The Colour of Iodides.

Dr. O. Silberrad—On Essential Oils.

Dr. R. H. Pickard—The Cholesterol Group.

Prof. A. Senier—On Acridines.

M. le Comte A. de Gramont—Sur le Spectre de Self-induction du Silicium et ses Comparaisons Astronomiques.

Prof. G. von Georgiewiecs—The Theory of Dyeing.

Dr. W. A. Bone—The Slow Combustion of Methane and Ethane. (A discussion ensued on the General Subject of Combustion).

Dr. J. T. Hewitt—Fluorescence as Related to the Constitution of Organic Substances.

J. E. Petavel and *R. S. Hutton*—Preliminary Note on some Electric Furnace Reactions under High Gaseous Pressure.

Holland Crompton—The Atomic Latent Heats of Fusion of the Metals, considered from the Kinetic Standpoint.

Dr. E. Perman—The Influence of Small Quantities of Water in bringing about Chemical Reactions between Salts.

Prof. W. N. Hartley—Report of Committee on Absorption Spectra and Chemical Constitution of Organic Substances.

Dr. J. C. Philip—Freezing-point Curves of Binary Mixtures.

Prof. T Purdie and *J. C. Irvine*—A Contribution to the Constitution of Disaccharides.

Dr. E. F. Armstrong—Mutarotation in Relation to the Lactonic Structure of Glucose.
W. Sloan Mills—Synthesis of Glucosides.
W. Sloan Mills—Preparation of Oximido-Compounds.
W. Sloan Mills—The Action of Oxides of Nitrogen on Oximido-Compounds.
W. Thomson—Further Investigation of Approximate Estimation of Minute Quantities of Arsenic in Food.
Dr. A. W. Crossley—Report of Committee on the Study of Hydro-aromatic Substances.
Dr. Marshall Watts—Report of Committee on Wave-length Tables of the Spectra of the Elements and Compounds.

The Chemical Laboratory at Wiesbaden.—During the Summer Term, 1903, the Fresenius Chemical Laboratory was attended by thirty-seven Students. Of these, twenty-seven were from Germany, two from Austria, one from England, one from Luxemburg, one from Holland, one from Switzerland, one from France, one from Russia, one from Transvaal, and one from Japan. There were three Assistants in the Instruction Laboratory, and twenty-four in the Versuchsstationen (private laboratories). To the certified staff of teachers belong the Directors, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Prof. Dr. Med. G. Frank, Dr. L. Grünhut, Dr. R. Fresenius, and J. Huber (Architect). The next Winter Term begins on October 15. During the Summer Term, 1903, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen), in the interest of trade, industry, mining, agriculture, hygiene, justice, and government.

Tungsten, Molybdenum, Uranium, and Titanium.—A. Stavenhagen and E. Schuchard.—The authors have obtained, by means of aluminothermy, alloys of WCo, WMo, MoV, MoFe, MoSb, UFe, UCo, UMn, TiFe, TiCo, TiCu, PbW, PbMo, FeBa, CrCuWMo, TiWMo, MoUCrTi, and FeMnU. Titanium cannot be obtained in a state of purity under these conditions. The easily reducibles oxides, like PbO, Bi_2O_3, ZnO, or HgO, when mixed with powdered aluminium, give rise to violent explosions. The experiments were carried out by mixing up the oxides with powdered aluminium moistened with alcohol in a crucible, and in the half-dried masses a few vent holes were pierced by means of a stirring-rod. After desiccation heat was applied either by means of electricity or by a flame, or even by smokeless gunpowder.—*Berichte*, vol. xxxv., p. 909.

Transformation of Hypochlorites into Chlorates.—F. Foerster.—In this research the method adopted was based on the following reaction: $HOCl + H_2O_2 = HCl + H_2O + O_2$, by means of which hypochlorite can be titrated in the presence of chlorate. The results of the experiments are as follows:—(*a*). The reaction $Cl_2 + H_2O + NaOCl = NaCl + 2ClOH$ does not take place, and no augmentation of the amount of active chlorine is observed under these conditions. (*b*). Quantitative estimations confirm the equation $\overset{-}{Cl}O + 2ClOH = \overset{-}{Cl}O_3 + 2\overset{+}{H} + 2\overset{-}{Cl}$ when we react with hypochlorous acid on a solution of hypochlorite. (*c*). The formation of the chlorate in solutions containing the same total hypochlorous Cl, but with a variable proportion of ClOH and ClONa.—It was observed that the concentration of the ClOH remained constant as long as any hypochlorite remained. The determination of the speed of the reaction showed that the transformation of the hypochlorite took place according to a mono-molecular reaction; the constant of the reaction for different concentrations of ClOH is proportional to the square of the concentration; dilution considerably increases the time necessary for the total disappearance of the hypochlorite. (*d*). The formation of the chlorate increases with the concentration of the NaCl; the neutral salts ($NaNO_3$, for example) act in the same manner. (*e*). Action of ClOH on the alkaline chlorides.—Among the neutral salts, the chlorides have a greater action than the other salts; if with $NaNO_3$ or $NaClO_3$, a solution of ClOH undergoes a loss of 6 per cent, in the case of NaCl of the same molecular concentration the loss is 40 per cent. Finally, the author shows that the low alkalinity observed by W. von Tiesenholt on evaporating a solution of ClOH, treated with NaCl, is due to the hydrolysis of the hypochlorite formed according to the equation of equilibrium: $NaOCl + H_2O \rightleftarrows NaOH + ClOH$.—*Journ. f. Prakt. Ch.*, vol. lxiii., p. 141.

Determination of Sulphur in Steel.—B. F. Weston (*Iron Age*).—The evolution method gives results 0·005 to 0·025 per cent low in pig- and cast-iron. G. T. Doughty has advocated annealing the drillings for fifteen minutes. The author has applied this annealing also to steel drillings of basic open-hearth steel. Results with 12 samples showed a gain of 0·0005 to 0·004 per cent sulphur by the evolution method, when the samples had been annealed fifteen minutes over a blast-lamp in a covered porcelain crucible. The average gain was 0·003 per cent.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Cut Potatoes—Would some reader be good enough to inform me the best way to preserve cut potatoes without destroying the germinating properties of the tuber. I am told there is some chemical with which the cut parts of the potato could be dressed that would stop the bleeding or dry up the cut parts. I am anxious to cut out the eyes of a new variety (to reduce the weight) to send abroad by Parcels Post.—Amateur.

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2287.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

Southport, 1903.

By Professor W. N. HARTLEY, D.Sc., F.R.S., F.R.S.E., President of the Section.

(Concluded from p. 145).

Absorption Spectra (*continued*).

Tautomerism.

The possibility of an atom of hydrogen occupying alternative positions in a compound—

$$(NH{\cdot}C{:}O \rightleftarrows N{:}C{\cdot}OH)$$

so that it may be united to an atom of nitrogen or of carbon in one instance, or to an atom of oxygen in another, easily gives rise to substances with different characters: the one that of a phenol, the other that of a ketone. One interpretation of the facts observed which has been very commonly received may be stated thus:—Certain compounds have in their constitution an atom of hydrogen of a "roving disposition" which at one time will attach itself to an atom of oxygen, or to an atom of nitrogen, and anon it will forsake one of these and unite itself to an atom of carbon. The consequence of this "instability of character" is that when a derivative of the compound is being prepared or sought for by a chemical process, which according to all previous knowledge ought to yield it, the substance brought forth is of a different class, but withal of the same composition; it is, in fact, an isomeride.

According to another theory, the two isomeric derivatives of the parent substance are present in equal proportions in a solution in a state of equilibrium, and upon crystallisation one or other of these assumes the solid form. Taking those cases where a substance has a constitution which it is believed has been correctly ascertained by chemical reactions, and which yields two isomeric alkyl derivatives, it becomes a question as to which of these the parent substance has directly given birth to. The evidence from chemical reactions has in many cases failed to give a satisfactory answer, but the curves of molecular vibrations of such substances afford the desired information concerning the relationship of their constitution to that of their respective derivatives.

Most convincing evidence has been afforded by observations on their spectra, that several of the parent substances are really not what they seem to be.

Thus, isatin and methyl pseudo-isatin yield curves which are almost identical, the sole difference between them being due to the substitution of the alkyl radical for hydrogen, the nature of which difference might have been predicted.

Clearly the parent substance and the pseudo-derivative are of the same nature and constitution.

Carbostyril and methyl pseudo-carbostyril, *o*-oxycarbanil and its ethyl ether, obtained by boiling with potash and ethyl iodide, are also similarly related, and they possess the ketonic or lactam structure.

On the other hand, methylisatin, carbostyril, and the other ether of *o*-oxycarbanil yield curves which are essentially different from the foregoing, and are enolic or of the lactim type. Generally speaking, the ketonic are more stable than the enolic forms. Dibenzoyl methane is ketonic, and the tautomeric substance oxybenzalacetophenone is enolic, and in this instance the enolic form is that with the greatest stability. The two substances yield different curves, and the gradual change of the less stable into the more stable form can be traced by photographing the spectra of the solutions at intervals.

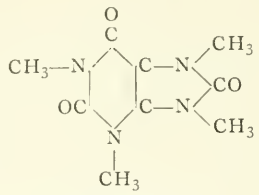
The ethyl esters of dibenzoyl succinic acid are of interest in this connection. There are three isomers known out of the thirteen which are possible, and the spectra of these have been studied. Knorr has given three formulæ for what he designates the α, β, and γ esters. Of these there are two, the β and γ forms, which give identical absorption curves: they are of the ketonic type, and structurally identical, but configuratively different, being stereoisomerides.

The curve of molecular vibrations of the α ester is quite different from that common to the β and γ compounds. The α compound is of the enolic type, and it changes spontaneously at ordinary temperatures into the ketonic, thus showing that in this case also the latter is the more stable. The transition from the one form to the other was seen to be in progress, and after an interval of only three hours the absorption band of the enolic ester had almost entirely disappeared. In three weeks the transformation had become complete, as was shown by the molecular vibration curve of the α ester being almost exactly coincident with that of the β and γ forms.

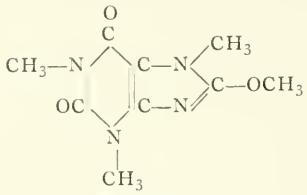
Another interesting example is afforded by the study of phloroglucinol, it being a substance with a constitution of a somewhat doubtful character, for owing to the ambiguity of its behaviour towards chemical reagents it is impossible to arrive at a decision from chemical evidence whether the oxygen atoms are present in enolic or ketonic groups. Towards some substances it behaves as a phenol, towards others as a ketone. The doubt also presented itself as to whether phloroglucinol from various sources had the same constitution, and, further, whether there might not be two isomeric forms of the compound present in equal proportions in a solution of the substance. Specimens of phloroglucinol prepared in five different ways from different materials gave curves of molecular vibrations which were identical: this decided the question absolutely; they are one and the same substance. If the constitution of the substance is that of a trihydroxybenzene or phenol, then the trimethyl ether should exhibit an absorption curve differing but slightly in detail from that of the parent substance; and, furthermore, the latter should exhibit a general resemblance to the curves of pyrogallol and phenol. This was found actually to be the case in both particulars.

Finally, with regard to tautomerism, it may be considered as decided that no evidence has been obtained based upon either physical measurements or chemical reactions of, first, the presence of a "wandering" atom of hydrogen as a characteristic of compounds which exhibit tautomerism; secondly, that solutions of tautomeric compounds do not contain equal quantities of the two substances, or enolic and ketonic forms in equilibrium, and that if both are present one so greatly preponderates over the other that no trace of any but the one compound can be detected; thirdly, it has been observed that some substances do change spontaneously from one form to another, and that this change sets in very quickly after the substance has been dissolved; fourthly, that substances change from one form to another under the influence of different reagents, as, for instance, cotarnine, as Dobbie and Lauder (1903) have shown, in presence of methyl alcohol or of caustic soda, and again in presence of potassium cyanide. In fact, it appears that, under the influence of different reagents, one or other of the two compounds is the more stable, and the more stable substance is then formed.

A reaction is recorded in the researches of Emil Fischer where it appears that two tautomeric forms are produced simultaneously from oxycaféine. When the silver salt of this substance is heated with methyl iodide it yields a mixture of tetramethyl uric acid and methoxycaféine, the characteristic groupings in which are —NH—CO— and —N=COH—, the hydrogens being methylated. This is a singular reaction which has not yet been studied spectrographically.



Tetramethyluric acid.



Methoxycaféine.

The Absorption Spectra of Alkaloids.

The interest attached to an examination of the absorption spectra of the alkaloids is not alone the fact that a means of recognising, detecting, and estimating such substances was devised, but still more that we may learn something of their chemical constitution. Many of the poisonous alkaloids give no distinctive chemical reactions, and in certain cases the means of recognising them are restricted to observations on their crystalline form and their physiological action. The physiological action of certain alkaloids of an extremely deadly character is remarkable enough to prove a means of their identification when the effect on the human subject is under observation. The first experimental work on the absorption spectra of the alkaloids arose out of a celebrated trial for murder, which engaged much attention in the year 1882. It was proved that the lethal drug administered was aconitine.

To identify this substance, of which there are several varieties, it was necessary at that time to resort to physiological tests made upon small animals.

Such a course always affords an opportunity for forensic arguments based upon the evidence adduced. To substitute absolute physical measurements for physiological tests seemed to present facilities for securing justice by removing any doubt of the identity of an unknown substance with the nature of one which is known. Alkaloids yield spectra of two kinds, those which do not and those which do exhibit absorption bands, the difference between the two classes of substances being one dependent on the constitution of the nucleus or ultimate radical of the compound. It is possible not only to identify substances, but also to determine the quantity present in a mixture or solution, and this has actually been done.

Alkaloids which are derived from benzenoid hydrocarbons, pyridine, quinoline, or phenanthrene give evidence of their origin by their spectra. It is therefore advantageous to make a careful study of the absorption spectra of the substances themselves and of the various products derived from them when studying their constitution. It was remarked while the work was in progress that the quinine spectrum curve was probably due to the conjugation of four pyridine or two quinoline nuclei. It is known now to be a substance of a complicated structure containing one quinoline nucleus. It differs from cinchonine only by one methoxyl group in the *para*-position. Observations made on simple bases differ from those made on substitution products, such as alkyl derivatives, in this respect, that the bases are the more diactinic, while addition products, such as hydrogenised compounds, and also salts of the alkaloids, such as hydrochlorides, are more diactinic than the simple bases. It was shown by the researches of Alder Wright that different preparations of aconitine can yield substances slightly differing in constitution. On examining them it was shown that these preparations yielded different absorption curves, the variations in which were due to differences in the constitution of the different preparations. To state a particular case of a well-defined character, the aconitine from *Aconitum napellus* and japaconitine from a Japanese aconite prepared by Alder Wright had practically the same absorption spectrum and yielded similar curves; but that of japaconitine was just what might be expected from a substance with a nucleus of a similar constitution, but about twice the molecular weight of aconitine; in other words, a condensation of two molecules of aconitine into one—namely, what was observed in the spectra of morphine and apomorphine, a much greater absorptive power with a similar absorption curve.

It was shown that japaconitine has a constitution modified in such a manner; it being, in fact, what was termed by Alder Wright a sesquiapoaconitine; and the formulæ given for these substances are respectively:—Aconitine, $C_{34}H_{47}NO_{11}$; japaconitine, $C_{66}H_{88}N_2O_{21}$, which is in agreement with the spectrum observations. It has, however, been supposed by Freund and Beck that the two substances are identical.

Strychnine and brucine are two alkaloids evidently closely related, but little is known about their constitution; both seem to contain a pyridine nucleus united to what is probably a pyrrolic nucleus, the two constituting a conjugated nucleus resembling that of quinoline. The difference between brucine and strychnine is said to be simply that the former contains two methoxyls. The absorption curves show a wider difference than this, and it was predicted that strychnine appears to be a derivative of pyridine, but brucine is more probably a derivative of tetrahydroquinoline, or an addition product of quinoline of the same character, since there is a remarkable similarity between the curves of the two substances. I would suggest that for the future evidence from their spectra be taken into account in studying their constitution.

Stereoisomerism in the Alkaloids.

Many alkaloids having the same formula are stereoisomerides, and those related in this manner exhibit molecular absorption curves which are identical. The following examples are quoted by Dobbie and Lauder (1903) as the result of their investigations:—Dextro-corydaline and inactive corydaline; narcotine and gnoscopine; tetrahydroberberine and canadine. Where two compounds are known to have the same formula, and one of these is optically active, the other inactive, it may be inferred, as Dobbie and Lauder have pointed out, that they are not optical isomerides if their absorption curves are different; thus canadine and papaverine have the same formula, but their absorption curves show that they are structurally different.

It is a general rule that substances which agree closely in structure exhibit similar series of absorption spectra, while those which differ essentially in structure show absorption curves which are different; and to this rule neither aromatic compounds, alkaloids, nor dyes and coloured substances form any exceptions. That this is so is easily understood from the theory of absorption spectra. It must, however, be distinctly understood that the essential feature of importance in all such investigations is the quantitative relation of the substance to its spectra, whether these relations are based upon equal weights of material or equimolecular proportions in solutions of given volume and thickness.

The relationship of morphine, $C_{17}H_{17}NO(OH)_2$, and codeine or methylmorphine, $C_{17}H_{17}NO.(OH)(OCH_3)$, was shown by their spectra, the latter being a homologue of the former. A similar instance has been investigated recently by Dobbie and Lauder. The resemblance between the spectra of laudanine, $C_{20}H_{25}O_4N$, and laudanosine, $C_{21}H_{27}O_4N$, confirms the view that they are homologous bases. The close agreement of their absorption curves with those of corydaline and tetrahydropapaverine clearly indicates a similarity in structure to that of these alkaloids, but the relationship of laudanosine to corydaline is probably

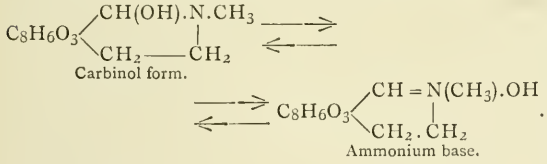
closer than to tetrahydropapaverine, and may be best explained by the formulæ—

$$\underset{\text{Corydaline.}}{C_{22}H_{27}O_4N} - CH_2 + H_2 = \underset{\text{Laudanosine.}}{C_{21}H_{27}O_4N}.$$

The removal of a methyl group from such a compound would scarcely cause any appreciable change in the curve of molecular vibrations, and very many cases are known where, when two atoms of hydrogen are introduced into a compound without altering the close linking of the carbon atoms of the ring formation in the compound, the alteration in the spectrum is insignificant.

A particularly interesting example of tautomerism already mentioned has been observed by Dobbie and Lauder in studying the constitution of cotarnine, a substance prepared from narcotine. Three formulæ have been proposed for it: one represents it as an aromatic aldehyde in which one hydrogen is replaced by an open chain containing nitrogen; a second gives it the character of a carbinol base; while a third that of an ammonium base. It has been supposed that in solution it is a mixture of two or all three such substances in a state of equilibrium, but as to what is the formula to be assigned to solid cotarnine the data are insufficient to determine. There are, however, two different solutions of the substance obtainable; that in ether or chloroform is quite colourless, like the solid; but a solution in water or alcohol is yellow. From the molecular absorption spectra of these solutions and of certain derivatives with which they are compared, there is very distinct evidence that a solution in alcohol or water contains the ammonium base, while under the influence of sodium hydroxide it assumes the condition of the carbinol form. Moreover, the rate of transformation and the conditions which influence this isomeric change have been studied. It suffices here to state that a solution containing entirely the one form may be converted wholly into the other.

The two formulæ referred to are given below:—



Emission Spectra.

Spark Spectra and their Constitution.

As it became necessary to make accurate measurements of absorption spectra in the ultra-violet, the work of obtaining the wave-lengths of lines in twenty metallic spectra was undertaken. They were for the most part in a region which, except in the case of two or three elements, had not been previously explored. A small Rutherford grating was employed, combined with quartz lenses with a focal length of three feet. Experience had shown that it was advisable in describing these spectra to give measurements in hundredths of an inch of the positions of the lines on the published photographs of the prismatic spectra in the *Journal of the Chemical Society* (March, 1882), and to follow Lecoq de Boisbaudran by giving a description of the character of each of the lines. In this way they are easily identified, and the value of the measurements for practical purposes is greatly enhanced. Prior to the publication of the work (1882), in the prosecution of which Dr. Adeney was associated with me, Liveing and Dewar, who had been engaged on a similar investigation, but operating in a different manner, published an account of the spectra of the metals of the alkalis and alkaline earths, and subsequently the lines of iron, nickel, and cobalt. They showed a rhythmic grouping of the lines to be characteristic of the spectra of the alkali metals.

In connection with the prismatic spectra which were photographed some remarkable facts were noticed; for instance, the character of the lines belonging to different groups of elements was a noticeable feature, as well also their disposition or arrangement, more particularly in the ultra-violet. Similarities in the visible spectra of zinc and cadmium, of calcium, strontium, and barium, and in those of the alkali metals had been observed by Mitscherlich, by Lecoq de Boisbaudran, and also by Ciamician. As to the grouping of the lines as observed on the photographs, it appeared that the spectra of well-defined groups of elements had characteristics in common which were different from those of other groups. For instance, the alkali metals differed from the alkali earth metals which appeared to form a group by themselves. Then in marked contrast to these simple spectra were those of iron, nickel, and cobalt, which though very complicated were seen to be much alike. Nearest to these but differing from them in certain respects were the palladium, gold, and platinum spectra.

It was observed how these elements with certain chemical and physical properties in common could be recognised as being relations owing to their family likeness when their spectra were photographed. Then it was remarked that the spectra of magnesium, zinc, and cadmium had distinctive characters in common; for instance, the individual lines in these spectra were marked by similar characteristics, such as a great extension of the strong lines above and below the points of the electrodes. This extension was increased with the atomic mass of the metal, and with the greater atomic mass in this group the volatility of the metal is also greater. An arrangement of the lines in pairs and triplets was noticed, the triplets being repeated, but less distinctly than in the first instance, and again repeated sharply but less strongly, so that there were three different sets of triplets in each spectrum. The point of greatest interest and importance was the connection traced between the atomic mass and the numerical differences observed in the intervals between the lines of different groups when measured by their oscillation frequencies.

These differences were not in the spectrum of one element, but were in the lines of each metal of the group, and were clearly associated with the atomic mass and chemical properties in each case.

The arrangement of the lines, which was common to all the metals in the magnesium, zinc, cadmium group, may shortly be described as follows:—Three isolated lines and one pair of lines in magnesium, with four sets of triplets; one isolated line and one pair of lines in zinc, with three sets of triplets; one isolated line and one pair of lines in cadmium, with three sets of triplets.

Besides the arrangement of these lines there were in the spectrum of each element two groups of the most refrangible lines, consisting one of a quadruple group and the other of a quintuple group, the groups and the lines composing them being similarly disposed in each spectrum. It was, however, not distinctly proved that these particular groups were strictly homologous, the most refrangible lines in the zinc spectrum being very difficult to photograph even on specially prepared plates, though the lines are strong. It was furthermore observed that with an increase in the atomic mass the distances between the lines, both in pairs and triplets, were greater. The same was the case with the quadruple and quintuple groups. In the magnesium spectrum, if we compare the first with the second group of triplets, we find the intervals extending from the first line in the first group to the first line in the second group, and from the second line in the first group to the second line in the second group, and from the third line in the first group to the third line in the second group, when measured in terms of oscillation frequencies, to be 677·1, 677·0, and 677·4. Similarly, taking the second and third groups, it is 391·2, 391·1, and 391·1. Between the third and fourth groups in like manner it is 230·9, 233, and 233; so that the intervals diminish with increase of refrangibility of the lines.

In the zinc spectrum the intervals between the lines in the first and second groups are 910, 910, and 910: in the second and third groups, 582, 581, and 583.

In the cadmium spectrum the corresponding intervals are 801·5, 800, and 800; in the second and third groups, 588, 589, and 587. The more accurately the lines are measured the more exactly do these differences correspond. It is scarcely necessary to point out that the differences in the atomic masses of the elements are in round numbers where H = 1, Mg 24, Zn 65, and Cd 112.

The Law of Constant Differences rendered it evident that the spectra of the elements were subject to a law of homology, which was closely connected with the atomic mass and with their chemical and physical properties.

It was, in fact, found, in accordance with the periodic law, that the spectra of definite groups were spectra similarly constituted, from which it was deduced that they are produced by similarly constituted molecules. It is evident that there is periodicity in their spectra. The metals studied being all monatomic in their molecular condition, the conclusion was inevitable that the atoms were of complex constitution, and that not only was the complex nature of these atoms disclosed, but it was also shown that groups of elements with similar chemical and physical properties, the atomic weights of which differed by fixed definite values, were composed of the same kind of matter, but the matter of the different elements was in different states of condensation, as we know it to be in different members of the same homologous series of organic compounds. If this were not the case, the mass or quantity of matter in the atom would not affect in the same manner its rate of vibration—which the facts observed lead us to conclude that it does—and the chemical properties of the substances would differ more widely from one another, and the differences between them would not be gradational, which in fact they are. It was thus impossible to believe that the atoms were the ultimate particles of matter, though so far as chemical investigations had proceeded they were parts which had not been divided. Here the conviction was forced upon one that matter might exist in a state which had hitherto been unrecognised by those who accepted the atomic theory without searching beneath it. All that the atomic theory enabled the chemist to take account of were the laws of combination and decomposition of the forms of matter that are ponderable and of sufficient mass to be weighable on the finest balances, which are after all but crude and imperfect instruments for the study of matter, since they are capable only of determining differences between masses of tangible size. It became conceivable that matter in the state of gas or vapour might become so attenuated that repulsion of the molecules would be greater than the attraction; that they would then no longer form aggregates, and in consequence would cease to be weighable. In such a condition they may be imagined to constitute the ether, and in view of this conception there may be recognised four physical conditions of material substances, namely, solid, liquid, gas, and ether.

It is more than twenty years ago since the study of homology in spectra led me to the conviction that the chemical atoms are not the ultimate particles of matter, and that they have a complex constitution.

That the atoms of definite groups of chemically related elements are composed of the same kind of matter in different states of condensation is not a dream or a view of a visionary character, for it is based upon definite observations controlled by exact physical measurements, and is therefore in the nature of a theory rather than an hypothesis. Batchinski (1903) regards the atoms as being in a state of vibration, and the periods of vibration of related elements appear to stand in a simple relation to their properties. The mass of an atom is proportional to the square of its period of vibration, and conversely the vibration period of the atom may be calculated from the square root of the atomic weight. These values have been calculated and arranged according to Mendeleeff's classification, whereby it is shown that there is a decided tendency to form harmonic series in the vertical columns. The deviations are probably capable of explanation, as the author believes, on the ground that the atom is not to be regarded as a material point, but as a material system. It is well to remember that the precursor of the Periodic Law was Newlands' Law of Octaves.

I have always experienced great difficulty in accepting the view that because the spectrum of an element contained a line or lines in it which were coincident with a line or lines in another element it was evidence of the dissociation of the elements into simpler forms of matter. In my opinion, evidence of the compound nature of the elements has never been obtained from the coincidence of a line or lines exclusively belonging to the spectrum of one element with a line or lines in the spectrum exclusively belonging to another element. This view is based upon the following grounds:—First, because the coincidences have generally been shown to be only apparent, and have never been proved to be real; secondly, because the great difficulty of obtaining one kind of matter entirely free from every other kind of matter is so great that where coincident lines occur in the spectra of what have been believed to be elementary substances, they have been shown from time to time to be caused by traces of foreign matter, such as by chemists are commonly termed impurities; thirdly, no instance has ever been recorded of any homologous group of lines belonging to one element occurring in the spectrum of another, except and alone where the one has been shown to constitute an impurity in the other; as, for instance, where the triplet of zinc is found in cadmium and the triplet of cadmium in zinc; the three strongest lines in the quintuple group of magnesium is graphite, and so on. The latest elucidation of the cause of coincidences of this kind arises out of a tabulated record from the wave-length measurements of about three thousand lines in the spectra of sixteen elements made by Adeney and myself. The instances where lines appeared to coincide were extremely rare; but there was one remarkable case of a group of lines in the spectrum of copper which appeared to be common to tellurium; also lines in indium, tin, antimony, and bismuth which seemed to have an origin in common with those of tellurium.

It is difficult to separate tellurium from copper, and copper from tellurium, by ordinary chemical processes. Dr. Köthner, of Charlottenburg, has succeeded in obtaining very pure tellurium from the spectrum of which these lines and also several others have been almost entirely eliminated, which shows that they are foreign to the element, and that his specimen of tellurium is probably purer than any previously obtained. For determining the atomic weight of tellurium it is of course necessary to obtain it in the greatest possible state of purity; and it may be mentioned that the material which Staudenmaier employed for this purpose was found, from Köthner's photograph of its spectrum, to be a very pure specimen.

The prosecution of researches in connection with the constitution of spectra was initiated by Johnstone Stoney, by Balmer with respect to hydrogen, and continued by Rydberg, Deslandres, Ames, and, above all, by Kayser and Runge, who by an eleborate and exhaustive investigation of the arc spectra of the elements have given us formulæ by which the wave-lengths of lines in the spectra of different elements in certain definite groups may be calculated. They also showed the spectra to be constituted of three series of lines, the principal series and two subordinate series, one sharp and the other diffuse.

Ramage, however, has given us a simpler formula depending on the atomic weight which applies to several groups, and he has co-ordinated the spectra of several of the elements with the squares of their atomic masses, and also their atomic masses with others of their physical properties.

It may here be remarked that the homology of the spark spectra in the magnesium, zinc, and cadmium series was at first called in question by Ames, though he proved the arc spectra of zinc and cadmium to be strictly homologous.

Preston decided the question by demonstrating by means of beautiful photographs that corresponding lines such as the pairs, triplets, and the quadruple groups in the

spark spectra of the three metals when under the influence of a very powerful magnetic field underwent the same kind of change; for instance, each quadruple group changed to sextuple, the second and fourth lines in each group becoming double. Lines in spectra which have not the same constitution behave differently. Recently, Runge and Paschen have arrived at the same conclusion; and, furthermore, have established homology in the spectra of sodium, copper, and silver; also between aluminium and thallium. Indium is almost certainly homologous with aluminium and thallium, but it was probably not investigated on account of its rarity. Marshall Watts has pointed out that a relationship exists between the lines in the spectra of some elements and the squares of their atomic weights, from which it is possible to calculate the atomic weight of an element if that of another in the same homologous series is known, and the oscillation frequencies of corresponding lines are known.

The knowledge of spectra we now possess enables the determination of atomic weights to be controlled with quite as much efficiency and certainty in many instances as by specific heat or vapour-density determinations.

The first application of the observed homology in spectra was directed towards the question of the atomic mass of beryllium, for which purpose the lines in the ultra-violet spark spectrum of this element were first photographed and measured. The nature of the evidence on the subject adduced at the time was in outline as follows:—

"If, as Nilson and Petterson suggest, the position of beryllium is at the head of a series of triad rare earth metals, the element scandium (at. wt. 44) and yttrium (at. wt. 89) must be members of the same group. If this be the case the spectra of the three elements must have certain characters in common, for the series of which aluminium and indium are the first and third terms yield strictly homologous spectra. As a matter of fact, no two spectra could be more dissimilar than those of beryllium and scandium."

Having compared the photographs and wave-length measurements of a large number of spectra of the elements, I felt justified in making the following remarks:—

"The spectrum of beryllium exhibits no marked analogy with the calcium, the magnesium, or the aluminium spectra, all of which are members of well-defined homologous series. There is nothing similar in it to the boron, silicon, or carbon spectra, nor to those of the scandium, yttrium, or cerium. The spectrum of lithium is most closely analogous to that of beryllium in the number, relative positions, and intensities of the lines. This leads to the conclusion that beryllium is the first member of a dyad series of metals, to which in all probability calcium, strontium, and barium, as a sub-group, are homologous, its atomic mass being 9·2, its place is above magnesium." Subsequently, Nilson, and also Humpidge, by chemical evidence and from vapour-density determinations of certain compounds, substantiated the conclusion previously arrived at by Emerson Reynolds, that the atomic mass of beryllium was not 13·8 but 9·2.

The next practical application of the spark spectra was to the analysis of rhabdophane, a mineral found many years ago in Cornwall, and described by Heuland in 1837 as a zinc blende of a peculiar character.

This mineral I found to contain neither zinc nor sulphur, and therefore it is not a blende. It is, in fact, a phosphate of the formula $R_2O_3.P_2O_5.2H_2O$, in which the oxides of cerium, didymium, lanthanum, and yttrium may wholly or in part replace each other. The didymium absorption spectrum is well seen both by reflection from the surface and transmission through thin sections of the mineral. The spark spectrum of the yttrium chloride obtained from rhabdophane was compared with that observed by Thalén and ascribed to yttrium. Of the fifty-one lines in the spectrum of yttrium thirty-eight were absent from the yttrium obtained from rhabdophane, and it was concluded that the purest yttrium was that which yielded the simplest spectrum. This was the first occasion of the finding of yttrium in any British mineral. Quite recently a confirmation of this view has been obtained by comparing this spectrum with lists of the arc lines of yttrium and ytterbium which have just been published by Kayser (1903).

Penfield analysed a mineral found in the United States which he named scovellite; it proved to be identical in species with rhabdophane.

Flame Spectra at High Temperatures.

What are commonly known in the chemical laboratory as flame spectra are chiefly those of the metals of the alkalis and alkaline earths; also of gallium, indium, and thallium. The researches of Mitscherlich and Lecoq de Boisbaudran first showed that copper, manganese, and gold gave flame spectra. Lockyer, Gouy, and Marshall Watts also investigated flame spectra.

In 1887 I used iridium wires one millimetre thick, twisted into loops upon which fragments of minerals were heated in the oxygen blowpipe flame. Natural silicates yielded spectra not only of alkalis but of the alkaline earths, and also distinct manganese spectra. Bartya, strontia, and lime gave spectra when insoluble compounds such as the sulphates were thus examined at high temperatures. Iron, cobalt, and nickel gave spectra even when compounds such as the oxides were heated strongly. But iridium, though infusible, is somewhat volatile, and contributes a line spectrum to the flame. In 1890 thin slips of the mineral kyanite and even pieces of tobacco pipe were used instead. Experience with this method of working went to show how the flame spectra of oxides of calcium, strontium, and barium could be separated from those of lithium, sodium, potassium, rubidium, and cæsium, as observed in the Bunsen flame. Furthermore, that even the most volatile of these substances could be made to yield a continuous colouration from a single bead of salt for a period exceeding fifteen minutes, and extending to one or two hours, so that measurements of the lines might be made with some degree of certainty.

In order to study the flames emitted from furnaces during metallurgical operations, and particularly from the mouth of Bessemer vessels, it became necessary to ascertain what really were the lines of the elements observed under different conditions at a high temperature, and accordingly systematic methods of study were developed from the previous somewhat tentative experiments.

In all the flame spectra obtained by the oxyhydrogen blowpipe the ultra-violet line spectrum emitted by water-vapour which had been discovered by Huggins and by Liveing and Dewar was visible on the photographs by reason of the combustion of the hydrogen in the hydrocarbon, or the hydrogen gas itself, when burnt along with oxygen. The flame spectra are always shorter than those obtained from the arc or from condensed sparks. After an extended examination of spectra produced by the oxyhydrogen blowpipe from solid substances, the knowledge obtained was applied to the examination of the flames coming from the Bessemer vessel during the "blow" during all periods from the commencement to the termination. These observations were made at the London and North-Western Railway Steel Works at Crewe; and at Dowlais, in South Wales. In collaboration with Mr. Ramage, a large number of these complicated spectra were photographed at the North-Eastern Steel Works, where the Thomas-Gilchrist process is carried out. The spectra were fully described and measured, with the result that every one of the lines and bands was accounted for. A new line belonging to potassium was discovered to have peculiar properties. Gallium was proved to be present in the Cleveland ore from Yorkshire, in the finished metal, in clays and in all aluminous minerals, even in corundum. Also, by very accurate determinations of the wave-lengths of its principal lines, gallium was proved to be a constituent of the sun. Moreover, it was found in several meteorites. Pure gallium oxide was separated, by analytical methods, from iron ores and other materials; and the proportion of the metal in the steel rails made by the North-Eastern

Steel Company, of Middlesbrough, was determined and found to be one part in thirty thousand. This Yorkshire steel is richer in gallium than any other substance from which it has been extracted; for instance, the Bensburg blende, supposed hitherto to be the richest ore, contains only one part in fifty thousand.

By observations on the spectra, the thermo-chemistry of the Bessemer process of steel manufacture was studied, and the temperatures attained under varying conditions were estimated. The demonstration of the great volatility of most metals, and of many metallic oxides in an undecomposed condition, at the temperature of the oxyhydrogen blowpipe and of the Bessemer flame, was of special interest. The metals chiefly referred to are copper, silver, lead, tin, manganese, chromium, iron, cobalt, nickel, palladium, gold, and iridium. Several of these, such as silver and gold, have lately been distilled *in vacuo* by Krafft.

Banded Flame Spectra.

Well-defined groups of elements yield banded flame spectra which have a similar constitution; thus magnesium, zinc, and cadmium yield bands composed of fine lines, degraded towards the violet, while fluted band spectra of beryllium, aluminium, and indium were found to be degraded towards the red. Thallium also yields a fluted spectrum; gallium gives a line spectrum; lanthanum gives bands degraded towards the red; palladium gives bands in the nature of flutings composed of fine lines; germanium gave very faint indications of bands; rhodium and iridium both lines and bands. It became manifest that elements belonging to the same group in the periodic system of classification exhibited banded spectra which are similarly constituted, and hence similarly constituted molecules of the elements have similar modes of vibration, whether at the lower temperature of the flame or at the higher temperature of the arc or spark. Banded spectra are thus shown to be connected with the periodic law.

A great advantage is to be derived from an investigation of banded spectra from a theoretical point of view, as well as from the application of this method to the analysis of terrestrial matter. While the spectra are easily obtained, they can be applied in a very simple manner to the chemical analysis of minute quantities of material, and may readily be made quantitative.

M. Armand de Gramont has described a method of obtaining spectra of metals and metalloids by means of a spark, and has given the analysis of eighty-six mineral species. The novelty and importance of his work lies in the method of obtaining spectra of such constituent substances as chlorine, bromine and iodine, sulphur, selenium, and tellurium; also phosphorus and carbon when in a state of combination, as sulphates, phosphates, carbonates, &c.

There is a possibility of utilising this method for the quantitative determination of carbon, sulphur, and phosphorus in iron and steel during the process of manufacture.

Definition of an Element.

In a discussion on the question of the elementary character of argon in 1895, it was pointed out by me that argon gave a distinct spark spectrum by the action of condensed sparks, and therefore, on this evidence alone, it must be regarded as an element. The fact that it gave two spectra under different conditions was not opposed to, nor did it invalidate, this evidence, because such an element as nitrogen not only emits two spark spectra, but the two spectra can be readily photographed simultaneously from the same spark discharge.

It was proposed by M. de Gramont, at the International Congress in Paris in 1900, and agreed, that no new substance should be described as an element until its spark spectrum had been measured and shown to be different from that of every other known form of matter.

This appears to me to have been one of the most important transactions of the Congress. The first application of this rule has resulted in the recognition of radium as a new element; it is characterised by a special spark spectrum of fifteen lines which have been fully studied and measured by Demarçay. It shows no lines of any other element.

Another application of this rule has recently been made by Exner and Haschek with preparations of the oxide of an element obtained by Demarçay, and named europium. It exhibits 1193 spark lines and 257 arc lines.

I have already mentioned that one feature strikingly shown in the spectra of chemically related elements was the wider separation of the lines in pairs, triplets, or other groups; was in some way related to the atomic mass, since the separation was greater in those elements whose atomic weights were greater. Kayser and Runge, and also Rydberg, have shown that in the series of alkali metals the differences between the oscillation frequencies of the lines are very nearly proportional to the squares of the atomic weights. Runge and Precht have recently shown that in every group of elements that are chemically related, the atomic weight is proportional to some power of the distance separating the two lines of the pairs of which the spectrum is constituted. In other words, if the logarithms of the atomic weight and distance between the lines be taken as coordinates, the corresponding points of a group of elements which are chemically related will lie on a straight line. Applying this law to the determination of the atomic weight of radium, they find that the strongest lines of the new element are exactly analogous to the strongest barium lines, and to those of the closely related elements, magnesium, calcium, and strontium. The intervals between the two lines of each pair in the principal series, and in the first and second subordinate series, if measured on the scale of oscillation frequencies, are equal for each element, and the same law holds good for the spectrum of radium. From this the value 257·8 was found for the atomic mass of the element. This does not quite accord with the number obtained by Madame Curie, who found it to be 225. It will be interesting to see which number will eventually be proved to be the more correct.

It is now many years since I first pointed out that the absolute wave-lengths of the lines of emission spectra of the elements are physical constants of quite as great importance in theoretical chemistry as the atomic weights; in the light of recent discoveries this statement may be said to be now fully justified.

Radio-active Elements.

From the study of rays of measurable wave-lengths we have lately sailed under the guidance of M. Henri Becquerel into another region where it is doubtful whether all the rays conform to the undulatory theory. In fact, some of the rays are believed to be charged particles of matter, charged, that is to say, with electricity. Beyond doubt they are possessed of very extraordinary properties, inasmuch as they are able to penetrate the clothing, celluloid, gutta-percha, glass, and various metals. They are, moreover, endowed with a no less remarkable physiological action, producing blisters and ulcerations in the flesh which are difficult to heal. It is an established fact that such effects have been caused by only a few centigrms. of a radium compound contained in a glass tube enclosed in a thin metallic box carried in the pocket.

From this we can quite understand that there is no exaggeration in the statement attributed to the discoverer, Professor Curie, by Mr. W. J. Hanmer, of the American Institute of Electrical Engineers, that he would not care to trust himself in a room with a kilogrm. of pure radium, because it would doubtless destroy his eyesight, burn all the skin off his body, and probably kill him.

It remains for me to express regret that without an undue extension of the time devoted to this address, it would have been scarcely possible to afford adequate treatment to the absorption spectra of inorganic compounds, particularly those of the rare earths, and such also as afford evidence of the chemical constitution of saline solutions; or of organic compounds closely related to coloured substances and dyes, the investigation of which leads to the elucida-

tion of the origin of colour, and serves to indicate the nature of the chemical reactions by which coloured substances may be evolved from those which are colourless.

Chemistry is popularly known as a science of far-reaching importance to specific arts, industries, and manufactures; but it occupies a peculiar position in this respect, that it is at one and the same time an abstract science, and one with an ever-increasing number of practical applications. To draw a line between the two, and say where the one ends and the other begins is impossible, because the theoretical problem of to day may reappear upon the morrow as the foundation of a valuable invention.

ADDRESS TO THE MATHEMATICAL AND PHYSICAL SECTION OF THE BRITISH ASSOCIATION.

SOUTHPORT, 1903.

By CHARLES VERNON BOYS, F.R.S.,
President of the Section.

THE first duty of every occupant of this Chair is a sad one. Year by year the record grows of those who have devoted their lives to the development of mathematical and physical science, of those who have completed their work. The past year has added many names to the record—more, it seems, than its fair share. The names include some of the most brilliant and active of our race, of those to whom this Association is deeply indebted, and also of our fellow workmen in other countries whose loss is no less to be deplored.

Lord Salisbury's devotion to the empire, of which this is not the occasion to speak, left him but little time for those scientific pursuits in which he took so keen an interest. Once, however, as President of this Association, he showed our members that, unlike the majority of our statesmen, science was not to him a phantom. His Address at Oxford will remain in the memories of all who heard it. The eloquence, the humour, the satire, the subtilty provided an intellectual treat of the rarest kind.

Of Sir George Gabriel Stokes and his work it is not possible for me to speak. Any attempt on my part to appreciate or gauge the value of the work of such a giant would be an impertinence. This can only fitly be done by one of our leaders, and Lord Kelvin has paid a fitting tribute in the pages of *Nature*. I can only record the fact that Stokes was for seven years Secretary, and twice President of this Section, and in 1869 was President of the Association.

Dr. Gladstone, for fifty-three years a member of this Association, was not only an unfailing attendant at our meetings, but an active member whose steady stream of original communications on subjects connecting physics and chemistry earned for him the designation of Creator of Physical Chemistry. His investigations on spectroscopy, refractivity, and electrolytics are known to every student of physics. His researches upon early metallurgical history, while of less importance to the progress of science, are none the less interesting. An ardent apostle of education, he was for twenty-one years a member of the London School Board, and three years Vice-Chairman. Dr. Gladstone was the first President of the Physical Society. He has been President of the Chemical Society, and at the last meeting of the British Association at Southport—as also in 1872—he was President of the Chemical Section. So long ago, he said, in urging the importance of science as a factor in education, that the so-called educated classes were not only ignorant of science, but had not arrived at the knowledge of their own ignorance.

It is not possible to pass on without paying a tribute, in which all who knew Dr. Gladstone will share, to his character no less than to his genius.

Sir William Roberts-Austen was probably one of the most active members that this Association has known. Not only had he for many years made the subject of metals and alloys his own, but he worked for the Association in many ways. At three meetings have audiences been charmed by his fascinating and brilliant evening lectures, all relating to metals. He was President of the Chemical Section at the Cardiff meeting in 1891, and not only did he perform these duties, but he accepted the more laborious and more thankless task, for which his unfailing courtesy and tact so well fitted him, of acting as our General Secretary for four years. His labours in the important field of research which he tilled were appreciated by numerous technical societies and institutions of which he was an honorary member, or had been president or vice-president. Many branches of the public service had the advantage of his skill and experience, which received the official reward in 1899.

Dr. Common's skill as a designer and constructor of instruments was well known. His instinct or judgment in producing planes and figured concave mirrors of great dimensions was rare, for this is an art almost unknown in the laboratory. His generosity and his valuable advice have been appreciated by many besides myself.

Rev. H. W. Watson, Second Wrangler and Smith's Prizeman in 1850, was a Vice-President of the British Association in 1886. Mathematical physicists are familiar with the joint work of himself and Burbury on "Generalised Co-ordinates," and with his mathematical articles.

In Otto Hilger, the brother of the late Adam Hilger, who between them brought to this country German thoroughness and French skill in instrument manufacture, we have lost one of our first and most valuable constructors. Noted for the high class of all the optical work turned out by the firm, Otto Hilger was not afraid of attacking the problem of manufacturing the Michelson echelon grating. This little bundle of glass plates requires for its success perfection and precision commensurable only with the genius of the inventor. This Otto Hilger supplied.

Dean Farrar, a life member of the British Association, whose activity lay in another direction, showed his appreciation of the value of science in education by appointing the first science master at Marlborough when he became headmaster in the year 1870. As I was a boy at the school at that time, I can speak of the incredulity with which such an announcement was at first received, and of the general feeling that such an action was akin to a joke. I was, however, by no means the only boy who hailed the news with delight. We devoured the feast of chemistry and physics put before us by Rodwell and the books which at once became available. Out of gratitude to the late Dean of Canterbury I recall this episode.

James Wimshurst, the inventor of the influence machine which has carried his name into every corner of the scientific world, was not a member of this Association, but he fostered and encouraged the scientific spirit in young men who, by good fortune, came to know him. I do not think I have heard anyone spoken of with such gratitude and appreciation as Wimshurst, by men who in their younger days were allowed the run of his well-equipped workshop.

James Glaisher, best known as a balloonist in the sixties, has died at the great age of ninety-three. The balloon ascent with Coxwell on September 5, 1862, when they attained the altitude of 37,000 feet, will long remain in the popular imagination, not on account simply of the great altitude, but by reason of the sensational account of their having been paralysed with cold, and of their being able to stop the ever-increasing ascent only by the presence of mind of Coxwell, who, with his limbs frozen, seized the valve rope with his teeth, and so let out the gas.

While this event remains in everyone's mind, the more prosaic work of Glaisher in astronomy, meteorology, and photography, when most of us were children, and many yet unborn, led to his being elected president of various learned societies.

He gave one of the evening lectures of the British Association in 1863, the subject being balloon ascents.

A. F. Osler, the inventor of the self-recording direction and pressure anemometer and rain gauge, whose active meteorological work was carried out in the first half of the last century, when he contributed papers to the British Association and the Literary and Philosophical Society of Birmingham, has died at the still greater age of ninety-five. He was Vice-President of the British Association in 1865.

Of other countries, America has lost Professor J. Willard Gibbs, a mathematical physicist whose very learned and original contributions to the knowledge of the world on the thermodynamical properties of bodies, on vectors, the kinetic theory of gases, and other abstruse subjects, have received the highest recognition that the learned societies of this country can bestow. Professor Harkness, the astronomer, and Professor Rood, the skilled experimental physicist of Troy, have also maintained the high standard that we now look for in American science.

Germany has lost Professor Deichmüller, Professor of Astronomy at Bonn, at an early age. Sweden has lost Professor Bjerknes, whose hydrodynamical experiments showing attraction and repulsion were so much admired when he performed them at a meeting of the Physical Society some twenty-five years ago. Switzerland has lost Professor C. Dufour, the astronomer; and Italy has lost Professor Luigi Cremona, a foreign member of this Association, Principal of the Engineering School in Rome, whose contributions to pure geometry and to its applications have made him famous.

Of the events of the last year, one stands out beyond all others, not only for its intrinsic importance and revolutionary possibilities, but for the excitement that it has raised among the general public. The discovery by Professor and Madame Curie of what seems to be the everlasting production of heat in easily measurable quantity by a minute amount of a radium compound is so amazing that, even now that many of us have had the opportunity of seeing with our own eyes the heated thermometer, we hardly are able to believe what we see. This, which can barely be distinguished from the discovery of perpetual motion, which it is an axiom of science to call impossible, has left every chemist and physicist in a state of bewilderment. Added to this, Sir William Crookes has devised an experiment, characteristic of him, if I may say so, in which a particle of radium keeps a screen bombarded for ever, so it seems, each collision producing a microscopic flash of light, the dancing and multitude of which forcibly compel the imagination to follow the reasoning faculties, and realise the existence of atomic tumult. Thanks to the industry and genius of J. J. Thomson, Rutherford and Soddy, Sir William and Lady Huggins, Dewar and Ramsay, and others in this country, besides Professor and Madame Curie and a host of others abroad, this mystery is being attacked, and theories are being invented to account for the marvellous results of observation; but the theories themselves would a few years ago have seemed more wonderful and incredible than the facts, as we believe them to be, do to-day. An atom of radium can constantly produce an emanation, that is something like a gas, which escapes and carries with it wonderful properties; but the atom, the thing which cannot be divided, remains, and retains its weight. The emanation is truly wonderful. It is self-luminous, it is condensed by extreme cold, and vapourises again; it can be watched as it oozes through stop-cocks or hurries through tubes, but in amount it is so small that it has not yet been weighed. Sir William Ramsay has treated it with a chemical cruelty that would well-nigh have annihilated the most refractory or permanent known element; but this evanescent emanation comes out of the ordeal undimmed and undiminished.

Not content with manufacturing so remarkable a substance, the radium atom sends out three kinds of rays, one kind being much the same as Röntgen rays, but wholly different in ionising power, according to the experiments of Strutt. Each of these consists of particles which are shot out, but they have different penetrative power; they are differently deflected by magnets and also by electricity, and the quantity of electricity in relation to the weight is different, and yet the atom, the same atom, remains unchanged and unchangeable. Not only this, but radium or its emanations or its rays must gradually create other bodies different from radium, and thus, so we are told, one at least of those new gases which but yesterday were discovered has its origin.

Then, again, just as these gases have no chemical properties, so the radium which produces them in some respects behaves in a manner contrary to that of all proper chemicals. It does not lose its power of creating heat even at the extreme cold of liquid air, while at the greater degree of cold of liquid hydrogen its activity is found by Professor Dewar to be actually greater.

Unlike old-fashioned chemicals which, when they are formed, have all their properties properly developed, radium and its salts take a month before they have acquired their full power (so Dewar tells us), and then, for anything we know to the contrary, proceed to manufacture heat, emanations, three kinds of rays, electricity, and gases for ever. For ever; well, perhaps not for ever, but for so long a time that the loss of weight in a year calculated, I suppose, rather than observed, is next to nothing. Professor Rutherford believes that thorium or uranium, which act in the same kind of way, but with far less vigour, would last a million years before there was nothing left, or at least before they were worn out; while the radium, preferring a short life and a merry one, could not expect to exist for more than a few thousand years.

In this time 1 grm. of radium would evolve one thousand million heat units, sufficient, if converted into work, to raise five hundred tons a mile high; whereas a grm. of hydrogen, our best fuel, burned in oxygen, only yields thirty-four thousand heat units, or one thirty-thousandth part of the output of radium. I believe that this is no exaggeration of what we are told and of what is believed to be experimentally proved with regard to radium; but if the half of it is true the term "the mystery of radium" is inadequate: the miracle of radium is the only expression that can be employed.

With all this mystery before us, which I must confess myself wholly unable to follow, I feel sure that members of the Association who are interested in the work of this Section will welcome the discussion, for which our secretaries have been able to arrange, and hear from the lips of Professor Rutherford the conclusions to which his researches have at present brought him. No one is more fitted than Professor Rutherford to open such a discussion, for no one has attacked the theoretical side with such originality and daring, or with such ingenuity of experiment.

As an example of the activity of mind and of research to which the activity of radium has given rise, I may mention the fact that the last number of the *Proceedings of the Royal Society* is wholly concerned with radium, there being four papers, all of the first importance, dealing with entirely different phenomena.

It is not my purpose to review these or the subject of radium generally; I am in no way fitted to do so. But I cannot well let the present opportunity pass of referring to another mystery of which a conspicuous example is now leaving us. I refer to the mystery of the comet and its tails. What is a comet? of what does its tails consist? Gravitational astronomy has told us for many years past that compared with the planets or their satellites a comet does not weigh anything. It weighs pounds or perhaps hundreds, thousands, or millions of tons; but in comparison with inconspicuous satellites it weighs nothing. Yet some of them as they approach the sun from remote regions begin to shoot out streamers which pour away as though repelled by the sun, not being left as a trail behind the comet, as is so often supposed. These streamers, ejected towards the sun, bend round and pour away at speeds which are enormous compared with that of the comet itself, thus producing the tail. Now these streams separate very often, and give rise to comets with two or three tails. Let me

read one paragraph from "The History of Astronomy," by Miss Clerke :—

"The amount of tail curvature, he (Olbers) pointed out, depends in each case upon the proportion borne by the velocity of the ascending particles to that of the comet in its orbit; the swifter the outrush the straighter the approaching tail. But the velocity of the ascending particles varies with the energy of their repulsion by the sun, and this again, it may be presumed, by their quality. Thus multiple tails are developed when the same comet throws off, as it approaches perihelion, specifically distinct substances. The long straight ray which proceeded from the comet of 1807, for example, was doubtless made up of particles subject to a much more vigorous solar repulsion than those formed into the shorter curved emanation issuing from it nearly in the same direction. In the comet of 1811 he calculated that the particles expelled from the head travelled to the remote extremity of the tail in eleven minutes, indicating by this enormous rapidity of movement (comparable to that of the transmission of light) the action of a force much more powerful than the opposing one of gravity. The not uncommon phenomena of multiple envelopes, on the other hand, he explained, are due to the varying amounts of repulsion exercised by the nucleus itself on the different kinds of matter developed from it.

(To be continued).

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 147).

Chapter II. (*continued*).

Determination of the Atomic Weight of Radium.

In the course of my work I determined at intervals the atomic weight of the metal contained in specimens of barium chloride containing radium. With each newly obtained product I carried the concentration as far as possible, so as to have from 0·1 grm. to 0·5 grm. of material containing most of the activity of the mixture. From this small quantity I precipitated with alcohol or with hydrochloric acid some milligrms. of chloride for spectral analysis. Thanks to his excellent method, Demarçay only required this small quantity of material to obtain the photograph of the spark spectrum. I made an atomic weight determination with the product remaining.

I employed the classic method of weighing as silver chloride the chlorine contained in a known weight of the anhydrous chloride. As control experiment, I determined the atomic weight of barium by the same method, under the same conditions, and with the same quantity of material, first 0·5 grm. and then 0·1 grm. The figures obtained were always between 137 and 138. I thus saw that the method gives satisfactory results, even with a very small quantity of material.

The first two determinations were made with chlorides, of which one was 230 times and the other 600 times as active as uranium. These two experiments gave the same figure as the experiment with the pure barium chloride. There was therefore no hope of finding a difference except by using a much more active product. The following experiment was made with a chloride, the activity of which was about 3500 times as great as that of uranium; and this experiment enabled me, for the first time, to observe a small but distinct difference; I found, as the mean atomic weight of the metal contained in this chloride, the number 140, which showed that the atomic weight of radium must be higher than that of barium. By using more and more active products, and obtaining spectra of radium of increasing intensity, I found that the figures obtained rose in proportion, as is seen in the following table. A represents the activity of the chloride, that of uranium being unity; M the atomic weight found :—

A.	M.	
3500	140	Spectrum of radium faint.
4700	141	
7500	145·8	Spectrum of radium strong, but that of barium predominating.
Order of magnitude, 10^6 ..	173·8	The two spectra of almost equal intensity.
	225	Only a trace of barium present.

The figures of column A must only be looked upon as a rough estimate. The calculation of the activity of strongly radio-active bodies is difficult, for many reasons which will be discussed later.

At the termination of the processes described above, I obtained, in March, 1902, 0·12 grm. of radium chloride, of which Demarçay made the spectral analysis. This radium chloride, in the opinion of Demarçay, was fairly pure; its spectrum, however, showed the three principal barium lines with considerable intensity. I made four successive estimations of the chloride, the results of which are as follows :—

	Anhydrous radium chloride.	Silver chloride.	M.
I.	0·1150	0·1130	220·7
II.	0·1140	0·1119	223·0
III.	0·11135	0·1086	222·8
IV.	0·10925	0·10645	223·1

I then re-purified this chloride, and obtained a much purer substance, in the spectrum of which the two strongest barium lines were very faint. Given the sensitiveness of the spectrum reaction of barium, Demarçay estimated that the purified chloride contained only the merest traces of barium, incapable of influencing the atomic weight to an appreciable extent. I made three determinations with this perfectly pure radium chloride. The results were as follows :—

	Anhydrous radium chloride.	Silver chloride.	M.
I.	0·09192	0·08890	225·3
II.	0·08936	0·08627	225·8
III.	0·08839	0·08589	224·0

The mean of these numbers is 225. They were calculated in the same way as the preceding ones by considering radium as a bivalent element, the chloride having the formula $RaCl_2$, and taking for silver and chlorine the values Ag = 107·8, Cl = 35·4.

Hence the atomic weight of radium is Ra = 225.

The weighings were made with a Curie aperiodic balance, perfectly regulated, accurate to the twentieth of a milligrm. This direct reading balance permits of very rapid weighing, a condition which is essential in the case of the anhydrous chlorides of radium and barium, which gradually absorb moisture, in spite of the presence of desiccating substances in the balance. The bodies to be weighed were placed in a platinum crucible; this crucible had been long in use, and its weight did not vary the tenth part of a milligrm. during the course of one operation.

The hydrated chloride obtained by crystallisation was placed in the crucible and heated till converted into the anhydrous chloride. When the chloride has been kept for several hours at 100° its weight becomes constant, and does not change even if the temperature is raised to 200°. The anhydrous chloride thus obtained constitutes, therefore, a perfectly definite body.

The following is a series of determinations on this point; the chloride (100 m.g.) is dried in the oven at 55°, and placed in a desiccator over anhydrous phosphoric acid; it then gradually loses weight, which proves that it still contains moisture; in the course of twelve hours the loss was 3 m.g. The chloride is replaced in the stove, and the

* Thesis presented to the Faculté des Sciences de Paris.

temperature raised to 100°. During this process, the chloride lost 6·3 m.g. in weight. After being left three hours fifteen minutes in the oven, it lost 2·5 m.g. more. The temperature was maintained for forty-five minutes between 100° and 120°, which caused a loss of weight of 0·1 m.g. Then after being kept for thirty minutes at 125°, the chloride showed no diminution in weight. Then, however, after thirty minutes at 150°, it lost 0·1 m.g. Finally, after being heated for four hours at 200°, it lost 0·15 m.g. During these operations the crucible varied from 0·05 m.g.

After each determination of the atomic weight, the radium was converted into the chloride in the following manner :—To the solution containing the weighed radium nitrate and excess of silver nitrate was added pure hydrochloric acid ; the silver chloride was filtered off ; the solution was evaporated to dryness several times with excess of pure hydrochloric acid. In this way the nitric acid is entirely removed.

The precipitated silver chloride was always radio-active and phosphorescent. In determining the amount of silver contained in it, I satisfied myself that no ponderable amount of radium had been carried down with it out of the solution. The method I pursued was to reduce the silver chloride precipitated in the crucible by hydrogen generated from dilute hydrochloric acid and zinc ; after washing, the crucible was weighed with the metallic silver contained in it.

I made another experiment which showed that the weight of radium chloride regenerated was the same as that before beginning the operation.

These verifications are not so reliable as direct experiments ; but they serve to indicate the absence of any significant error.

From its chemical properties, radium is an element of the group of alkaline earths, being the member next above barium.

From its atomic weight also, radium takes its place in Mendeleeff's table after barium with the alkaline earth metals, in the row which already contains uranium and thorium.

Characteristics of the Radium Salts.

The salts of radium, chloride, nitrate, carbonate, and sulphate resemble those of barium, when freshly prepared, but they gradually become coloured.

All the radium salts are luminous in the dark.

In their chemical properties, the salts of radium are absolutely analogous to the corresponding salts of barium. However, radium chloride is less soluble than barium chloride ; the solubility of the nitrates in water is approximately the same.

The salts of radium are the source of a spontaneous and continuous evolution of heat.

Fractionation of Ordinary Barium Chloride.

We have endeavoured to determine whether commercial barium chloride contains small quantities of radium chloride, which escape detection with the means of estimation at our command. For this purpose, we fractionated a great quantity of commercial barium chloride, in the hope of thus concentrating the trace of radium chloride if such were present.

Fifty kilos. of commercial barium chloride were dissolved in water ; the solution was precipitated by hydrochloric acid free from sulphuric acid, which yielded 20 kilos. of the precipitated chloride. This was dissolved in water and partially precipitated by hydrochloric acid, which gave 8·5 kilos. of precipitated chloride. This chloride was fractionated by the method used for the barium chloride containing radium ; and at the end of the process, 10 grms. of chloride were obtained, corresponding to the least soluble part. This chloride showed no radio activity ; it therefore contained no radium ; this substance is, consequently, absent from the ores of barium.

(To be continued).

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month ending August 31st, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Charles Perrin, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, September 10th, 1903.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Aug. 1st to Aug. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes ; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during August has continued to be excessive. The actual amount of rain measured is 3·34 inches ; the average rainfall is 2·38 inches ; this gives an excess of 0·96 inch, which, added to the previous one of 8·81 inches, makes a total excess for the year of 9·77 inches, which is 62·3 per cent in excess of the thirty-five years' average. Notwithstanding this unprecedented rainfall the soluble organic matter in the Thames-derived supply, which has been exceptional in amount during the last few months, has now sunk considerably. The organic carbon per gallon, which in June was 0·189 and in July was 0·155, was reduced in August to 0·148 grain—only a trifle in excess of the average amount over the whole of last year, an exceptionally dry one.

Our bacteriological examinations of 370 samples taken during the last month have given the results recorded in the following table. Besides these samples we have examined 360 others from special wells, standpipes, &c., making a total of 730 samples in all :—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	270
New River, filtered (mean of 71 samples) ..	15
Thames, unfiltered (mean of 25 samples)	10,910
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 200 samples)	43
Ditto ditto .. .. highest	372
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 24 samples) ..	189
River Lea, from the East London Water Company's clear-water wells (mean of 25 samples)	33

Of the 296 daily samples taken from the filter wells of the Metropolitan Water Companies, five samples, or 1·6 per cent, were sterile. There were thirty-eight samples, or 12·8 per cent, containing more than 100 microbes, and of these, nineteen samples contained more than 150 microbes per c.c. The thirty-eight excess samples contained an average of 180 microbes per c.c. ; in July ten excess samples contained an average of 159 microbes per c.c

When we take into consideration the entirely abnormal weather experienced during the present summer, the con-

ditions of the supply from the bacteriological point of view must be pronounced, on the whole, satisfactory.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

NOTICES OF BOOKS

Synthesen in der Purin- und Zuckergruppe. ("Syntheses in the Purin and Sugar Groups"). By Emil Fischer. Braunschweig: Friedrich Viewig und Sohn. 1903.

The application of synthetic methods to the solution of biological problems is continually becoming more extended, and apparently fruitful of results, and the questions briefly touched upon in this lecture, which was delivered before the Swedish Academy of Science in Stockholm in December, 1902, cannot fail to excite the interest of all into whose hands it falls. The difficulties of explaining the outlines of such a subject as the above to a mixed audience, not composed of specialists, might fairly be regarded as almost insurmountable, but this able popular exposition shows what an enthusiastic lecturer can do, and the admirable blending together of history, experimental truth, and inspired forecast forms the type of lecture most likely to appeal to the critical faculties and imaginations of the hearers. Butlerow's and Kiliani's famous researches on the sugars are briefly described, with special reference to their applications to such questions as the action of the enzymes and the assimilation of the carbon dioxide of the atmosphere by plants, and nothing could show more plainly the powers of the great master of organic chemistry than the excellence of this lecture on a difficult, and, from some points of view, an abstruse subject.

Cyanid-Prozesse zur Goldgewinnung. ("Cyanide Processes for obtaining Gold"). By Manuel von Uslar and Dr. Georg Erdwein. Halle-a-S.: Wilhelm Knapp. 1903.

This book deals with the various modifications of the cyanide process, which may truly be said to have influenced methods of gold extraction to an extent only comparable in the metallurgical world to that of the Bessemer and Thomas-Martin processes in the iron and steel industries. Considerable space is devoted to the consideration of the chemistry of the changes involved in the process, which is well explained, and the most minute details of the many modifications of the original method are recorded. The information relating to the cost and output of the process has been drawn in all cases from reliable sources, and includes the description of the plant of some of the most important mines in the Transvaal. This volume appears to be quite up to the level of the preceding in the series of Monographs on Applied Electrochemistry, and experts will find it a very complete and useful guide.

Mechanism of the Substitution of Bromine.—Ludovik Bruner.—It is known that the presence of a little iodine facilitates the substitution of bromine for hydrogen in aromatic compounds; the author, examining the mechanism of this reaction, explains it by means of the dissociation of the bromide of iodine, and the bromising action of the atoms of free bromine which result from it. He examined more particularly the bromisation of benzene in the presence of iodine, and proved that its progress was that of a quadrimolecular reaction, $C_6H_6 + 4Br = C_6H_5Br + HBr_3$. He examined also the catalytic action of some other "bromine fixers" on the coefficient of speed. In some cases he measured the relative speeds of instantaneous reactions, and showed, in so far as it concerns the bromisation of phenol, of bromophenols, and of aniline, the parallelism existing between the speed of the reaction and the electrolytic dissociation. —*Zeit. Physik. Ch.*, vol. xli., p. 413.

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ADDRESS TO THE MATHEMATICAL AND PHYSICAL SECTION OF THE BRITISH ASSOCIATION.

Southport, 1903.

By CHARLES VERNON BOYS, F.R.S.,
President of the Section.

(Concluded from p. 159).

It is impossible not to be struck by the similarity both of phenomenon described and of language used in this paragraph and in almost any of the papers on radium. I know this mere superficial similarity is worth very little, if anything; but for centuries the sky has shown us a phenomenon still not entirely understood, and the inability to remove all difficulty by the aid of radium or similar material is no reason for dismissing the idea of connexion without further thought.

The comet's tail is still a mystery. Let me take the most recent explanation, which was set forth only three months ago in the *Astrophysical Journal* in the United States. Those admirable experimentalists Nichols and Hull have for some years been investigating the back pressure exerted by the action of light upon bodies on which it falls. In this they have followed the Russian physicist Lebedew, but in minuteness and delicacy of measurement, and in their successful elimination of disturbances, their results are unequalled. It is sufficient to say that, difficult and minute as the experiment is, their success is such that the discrepancy between the calculated force and that which they have found is under 1 per cent. Perhaps I may express some satisfaction that in this measurement use was made of the quartz fibre.

Having now definite and accurate confirmation of the existence of the force produced by the action of light, or rather radiation, Nichols and Hull proceed to examine the question as to how far such repulsion may be competent to overcome the gravitative attraction of the sun and drive away the matter which pours out from the comet. It is interesting to note here that Kepler put forward this very idea, and that Newton, the inventor of the corpuscular theory of light, looked upon the suggestion with some favour.

Coming now to this recent paper of Nichols and Hull, we find first the consideration of the relation of the attraction by gravitation, and the repulsion by light upon particles of different sizes and densities. Density has no influence on the action of light, while it is favourable to gravitation, and therefore unfavourable to tail formation. Size is favourable to both, but more to gravitation than to light, for if the diameter of a particle be doubled, one is increased eightfold and the other only four. So size favours gravitational attraction. Conversely, of course, smallness favours repulsion by light, which relatively should get greater and greater as the particles diminish in size. At last, then, a degree of smallness may be reached in which the repulsion by light will actually be equal to the attraction by gravitation, and such a particle would remain in space, its motion unaffected by our sun. Let the diminution of size continue, and then the repulsion will be in excess, and if the law were to continue it would with sufficient diminution become relatively as large as we please.

The law, however, does not continue. Schwarzschild has shown that when the particles are small enough, light does not act upon them in the same way. Owing to diffraction, the effect of light is unduly great for a certain very small size of particle, while it fails almost entirely when the particle is made much smaller. Thus it is that the indefinite increase in the repulsion by light as compared with the attraction by gravitation with diminution of size of particle is checked, and when, according to theory, with a particular density of particle, the light pressure is about twenty times as great as gravitational attraction, further diminution of size ceases to favour the action of light, and it begins to fall off again. The distance of the particle from the sun has no influence upon the relation between the two kinds of forces, for they rise and fall together. Nichols and Hull, therefore, while not denying that other causes may operate, believe that light pressure is adequate to account for the phenomena, and that where the material coming from the head or comet proper is of two or three kinds, whether of density or of size of particle, the separation of the two or three tails should naturally follow.

This theory presupposes that the nucleus of a comet will be able, owing to the evolution of gas under the sun's heat, to send out enormous quantities of dust, the finer and lighter the better, so long as it is not unduly small with respect to a wave-length of light. Such dust would account for any reflected solar light that the spectroscope may show, but it is not easy to see how the spectrum of hydrocarbons, of sodium, and of other metal, should be produced for lack of temperature. It is not easy to see why fortuitous dust should be graded of such sizes as to give well separated and defined tails; it is not easy to see how the dust could be produced in sufficient quantity to provide visible illumination to millions of millions of cubic miles of space through which it may be passing at ultra-planetary velocity, even though in looking through a million miles or so one grain of dust in a hundred miles might suffice to supply the light.

Other theories of the comet's tail require an electrified sun, the existence of which is explained by Arrhenius as being caused by the emission by the sun of negatively charged electrons which, picking up condensing gases as Aitkins's dust picks up moisture from the atmosphere, are driven away by the light pressure. Arrhenius believes that these acting on the matter in the tail would give rise to the bright line spectra which have been observed. The result of all this escape of negative electricity is a positively charged sun, but what limits the charge in the sun it is difficult to see, as it is, why the electrostatic attraction helped by gravitation does not ultimately stop the action. I may be displaying my ignorance, of which I am sufficiently sensible, but I am not aware of any evidence for the existence of the stream of electrified rains or drops imagined by Arrhenius.

Nichols and Hull, while calling to their aid the researches of Schwarzschild to give them a repulsive force some twenty times as great as gravitative attraction, do not seem to have given due weight to the extremely small range of size of particle for which this high effect is available. The maximum effect for any wave-length, according to Schwarzschild, is produced when the size is such that a wave-length will just reach round it; that is, with ordinary light when the diameter is between one hundred thousandth and one hundred and fifty thousandth of an inch. If the diameter is two-and-a-half times the wave-length, the action of light is only equal to gravity with a material of the density of water; or, again, if it is reduced to one-eighth of a wave-length it again becomes equal, and in these two cases there is no resultant action. With either larger or smaller particles gravity rapidly gets the better of light, while the high advantage of light over gravity is confined to very narrow limits.

What the sifting process can be that will give rise to such a quantity of this microscopic dust we can hardly expect to be told, nor why even if the material should in some mysterious way be graded, the ungraded wave-lengths of the solar spectrum should allow of the marked separation in some instances of comets' tails.

One thing, however, they do assert, and that is that the

light pressure can have no action on a gas, so that if what we see is considered to be gaseous the light pressure theory must be thrown over for some other.

I cannot leave this excursion of Nichols and Hull into a speculative domain of science without expressing my admiration of the experimental work which they have accomplished, or of my appreciation of the ingenuity and daring with which they have attempted the hitherto unheard of feat of making a comet.

While the theory just referred to may be the most recent, it must not on that account be supposed to displace all that has gone before; the authors themselves do not suggest this; it is the last thing that would occur to them. They have referred to the researches of Bredechin that occupy so large a proportion of the annals of the Observatory of Moscow.

It is impossible to read even a tithe of these without feeling that the subject of comets and their tails is one which Bredechin, by his amazing industry, has made his own property, and that any stranger casually passing by and taking a random shot should receive the severe penalty awarded to poachers in this country. Bredechin has dealt unmercifully—I do not say unjustly—with the author of at least one such random theory.

It is therefore with the greater diffidence and more urgent plea for forbearance that I venture to draw certain parallels and hazard certain suggestions which I admit freely have not reached a stage at which detailed comparisons with known comets are possible.

It does not seem possible now to contemplate the phenomena of the comet, of the divided tails, of their tenuity and transparency, of the pale luminosity, partly reflected solar light, partly light as from a glowing gas; of the gradual wearing out and disappearance of those comets which constantly pay visits to solar regions, with all the mysteries of radium now so much in evidence without tracing the features in which they resemble one another. By radium, of course, I mean any material with the remarkable radio-active properties that radium exhibits with such pre-eminent splendour, whether known in the laboratory or not.

How many physicists have been peering at comets through radium spectacles, or how many astronomers detect the sparkle of radium in the fairy tresses of their hirsute stars I know not. One writer, however, T. C. Chamberlin, so long ago as July, 1901, looked upon a connexion between radio-active materials such as were then known and comets as at least worth considering. Chamberlin's paper in the *Astrophysical Journal* was mainly on the tidal disruption of gravitating bodies and the possible evolution of comets, nebulæ, and meteorites, and he did not pursue this consideration in any detail; indeed, the enormous accumulation of new properties of radium was not then available.

Whatever may be imagined as to the constitution of a comet, difficulties still remain. All I suggest now is that the curious properties of radium and of similar bodies should be kept in mind. Radium at least supplies the means by which, if the increasing warmth or the tidal action of the sun should awaken its activity, Rutherford's α-rays should be shot out at the speed that he has measured of a thousand million inches a second, *i.e.*, one-twelfth the velocity of light. These α-rays, according to Rutherford, consist of helium; they weigh each twice as much as a hydrogen atom, and so the same weight of comet matter that would make one of Nichols and Hull's best particles, *i.e.*, one that would be just visible with a microscope, would be sufficient for about 400 millions of Rutherford's α-ray particles, an advantage surely where diffuseness seems so miraculous.

These particles, shot out at a velocity one-twelfth that of light, go so fast that, if they were to start horizontally on the surface of the earth, the gravitative attraction of the earth would curve their path to the infinitesimal extent of a curve with a radius of forty-thousand million miles. Yet so great is the electric charge they carry that a visible curvature can be imposed upon them in a practicable electrostatic field.

Now imagine these transferred into space at a distance from the sun, for instance, equal to that of Venus. Gravity there due to the sun is only one-thousandth of what it is here, so gravity there would be, to the same extent, less able to impose visible curvature on their paths. But their electric charges are still available, and unless I have made an arithmetical blunder of a considerable order, it would require no very heavy electrification of the sun to bend these rays round in a curve with a radius of 1000 miles. An electrostatic field of under two ten-thousandths of a unit should be sufficient, a field which would be produced if the sun were only charged with a surface density of one electrostatic unit on every three square centimetres.

Whether these figures are correct or not—and I know the risk of getting just thirty-thousand-million times too large or too small a result—does not much matter. An electrified sun, which after all others besides Arrhenius have postulated, would be sufficient to turn the rays and send them away at rapidly increasing speed so as to form the tail. The speed would in a short time reach the velocity of light if it were not for the change in properties of matter which supervenes when any such velocity is nearly reached. Thus, according to the ratio of charge to mass, particles such as Rutherford's α-rays would be sent away each with its limiting velocity, giving rise to streaks more or less well-defined, and double, triple, or multiple according to the number of kinds of ray which the various radio-active materials were able to generate.

Not only should streaks pointing away from the sun be formed, but any negatively charged rays, such as radium is said to give out, should form a tail directed towards the sun. Perhaps this might be expected to be general, but while not common one was described by Hind in the comet of 1823-24, and three or four more have been observed.

The head or coma would be the envelope of all the independent orbits, leaving the nucleus in all directions—orbits which, while their velocities are still of the Rutherford order, would be hyperbolas convex to the sun.

If this should not appear to be absolute nonsense it it would seem as if another difficulty should become less than it has been. I refer to the visibility, luminosity, and spectral character.

Lodge, as an interpreter of Larmor, tells us that an electrified ion subject to acceleration, whether transverse or in the line of motion, radiates energy. The streamers from the nucleus subject to the greatest acceleration may be bright almost as the nucleus itself; then, as they have become dissipated into regions where far less acceleration becomes possible, the radiation falls off and the tail is lost in space.

The observations made last month by Sir William and Lady Huggins of the spectrum given by a piece of radium in the air may have some bearing upon the luminosity of the comet. It is possible that the internal motions set up by the separate parts, each pursuing its individual orbit, may produce collisions numerous and violent enough to account for all the light that is seen, and for temperature sufficient to bring out the spectral lines that have been identified. Whether this is so or not, radio-active bodies and their emanations can produce light independently of such action; and now these observers have found that in the case of radium in air this light gives the spectrum, line by line, of nitrogen. It is possible that the enveloping nitrogen has had its atoms so harried by the activity of the radium as to give a response hitherto only awakened by electric discharge? The ability to obtain such a response opens up a new possible interpretation of these spectra, which hitherto have been assumed, with our laboratory experience only to guide us, to have required for their production temperature above a red heat. If further observations should confirm this, the hydrogen, the hydrocarbon, and possibly even the sodium or iron spectrum that has been observed, may have come from cold atoms; and it is not even quite beyond the limits

of imagination to picture, not from the comet matter itself, but from loose residual and highly attenuated matter through which the comet is passing.

There is one other feature of this remarkable observation of equal interest. The lines of the spectrum were not exactly in their proper place, but were all shifted towards the red end of the spectrum about twice the distance between the D lines. If only one or two lines had been so observed a different origin might well have been suspected; but when the whole series are faithfully reproduced it is reasonable to look upon the spectrum as modified to that extent as though the works of the nitrogen atom had not only been set in movement, but had been loaded with the radium emanation.

Before dismissing these random speculations on the possible connexion between radio-activity and comets I would ask your leave to refer once more to Bredechin's conclusions. He has found that it is merely necessary to postulate three kinds of matter, issuing from the nucleus with three initial velocities, and subject to repulsion from the sun with three sets of forces of repulsion—*i.e.*, as compared with ordinary gravitative attraction—for the whole of the phenomena of all sorts of comets to be very completely accounted for. His highest initial velocity is only about five miles a second, and his lowest about a quarter of a mile a second. His highest repulsion, after deducting gravitative attraction, is only eleven times gravity, and his lowest only a fifth of gravity. If, then, with such velocities and forces the phenomena can be exactly accounted for, it would seem futile to consider the possibility of initial velocities from 4000 to 80,000 times as great and effective repulsions of a corresponding order being able to produce effects with anything in common. This is not necessarily the case, for with the comparatively slow separation of the atoms of Bredechin's matter from the nucleus, each one describing its own hoperbola convex to the sun, the tail at any moment represents the then position of any number of atoms which left the nucleus for some distance back, whereas with the enormous velocities and effective forces now discussed the comet moves so slowly in comparison that the tail would practically represent the path at the time.

It has taken me far longer to throw out this not very luminous ray than I had expected or than it is worth. I fear that it is a sort of ray in which the ratio of its dead weight to its vitalising charge is too small to enable it to penetrate the lighest screen of examination.

These are the days of rays, and now before we have quite become familiar with the rays of radio-active bodies Blondlot has presented us with N rays which issuing from the mantle of an incandescent gas-burner penetrate wood or aluminium, and then increase the light without increasing the heat of hot bodies on which they fall.

Passing now from the amusement of speculation to more serious duties, I find myself confronted with the difficulties that prevent us in this country from succeeding as we used to do in the international struggle—a struggle the issue of which is daily becoming more and more a question of brains, of education, of skill and enterprise in manufacture—and finally of that great virtue extolled by the President of the United States, strenuousness.

It is the duty of everyone who sees the way in which we are being outstripped in the race to do what in him lies to scrape off the rust which is clogging our educational machinery. I now refer to the defects which hamper the intellectual progress of the majority of our youth. I believe the public school mathematics in this country stands on a level of its own, well below that of any other. In England, owing to our complicated system of weights and measures, which our Ministers and our Parliament dare not abolish for our own good, the scanty hours allowed for mathematics are devoted to the learning of tables which should never have to be learned at all, to compound reductions designed merely to puzzle but not to lead to any new step; and, even if our present system were not futile enough, to learning lists of antique values which serve the useful purpose of giving the boys something to do. The result is that beyond having time to acquire a few elementary algebraical rules the boy is never introduced to algebra proper; he has no idea of algebraical reasoning; his trigonometry often does not exist, and the very sound or suggestion of co-ordinate geometry or of the differential calculus, which might be well within his reach, produces a shiver of dismay. Geometry is presented for the first time in the form of Euclid, a form as repulsive to most boys as it well could be. I must confess to having been attracted and not repelled by Euclid; but the boy does not care for time. Now that I look at Euclid again I have also to confess that any lingering regard for an old friend vanishes before the archaic language and the unnecessary circumlocution. If Euclid must be retained let it be translated into English, the English hat any parent would use in explaining the ideas to his son; let it be illustrated by constant reference to real things so as to appeal to the boy who does not revel in the abstract. Let the ideas and the terms first be presented in the form of experiments and of measurements with instruments; let the schoolmaster dare to throw over the intolerable conservatism which prevents our doing anything ten times as well lest some item should prove to be a trifle worse; in fact, let us take some heed of the possibly extreme, but none the less genuine, and valuable preaching of Professor Perry. I have so far referred only to the miserable use that is made of the odd hours grudgingly given to what is called mathematics. Is it any use to repeat the long-standing complaint of the way in which the schoolmaster insists upon overdoing his Latin and Greek under the belief that they are at least essential to intellectual development if, indeed, they do not supply the only stimulus? As society is constituted they are essential to education as an extensive knowledge of Confucius is essential to an educated Chinaman, so that we may mix one with another, appreciate the works of our great authors, understand the same allusions, and have the same kind of knowledge of the development of our civilisation. Few men of science, perhaps none, wish to see all of this, some of which is essential to a general education, abolished; all that we ask is that the schoolmaster shall not continue to impose upon the community the unbalanced learning which corresponds to mathematics and science without letters. The time given to classics is exorbitant; more must be reserved for those pursuits which draw out the habit of independent thought, creation, and originality. It would be well if every schoolmaster could read an admirable article by James Swinburne on the two types of mind fostered by the two complementary types of education, but this is buried away in an inaccessible number of the *Westminster Review*.

The classic is unfortunately still in possession, and where, as is still often the case, he is innocent of any appreciation of the educational value of post-Newtonian studies it is not surprising that he thrusts into odd moments the subjects he does not understand, and which he therefore despises, and that the boys committed to his charge and living in such an atmosphere are half ashamed of showing any interest in the scanty science which is within their reach. It is almost impossible to believe that such can be the case, but I have referred to the impression to which the appointment of the first science master at my own school gave rise. I now refer to the contribution to a discussion on education but a year or two ago by that experienced teacher, Principal Griffiths. Fortunately our public schools are not the only ones in the country. Smaller and less fashionable schools pay more attention to education and suffer less from what, in defiance of all rule, I can only call didactatorial method.

I am not aware that the result of this almost total exclusion of tabooed subjects in favour of Latin and Greek is producing a standard of classical attainment in our youth greatly in advance of that to be found in other countries, but it is certain that in history, modern languages, mathe-

matics, and science the product of our public schools is sadly deficient.

There is another point related to our deficient general scientific training on which I wish to offer some remarks, and that is in relation to manufacture. It is the fashion among some of our scientific people to talk of our manufacturers as if they were a very ignorant lot and to suppose that one word from some professor who has never seen outside a laboratory would be sufficient to put them right. Now in my somewhat varied experience I have had occasion to become acquainted with corners of our great manufacturing areas, and while my experience is small and not enough to generalise upon, it is nevertheless several times as great as that of some who are ready to adopt the superior attitude, but have none.

The loss of one industry after another is only too patent. In so far as this may be due to want of enterprise in our men of business we are not concerned with the cause in this Section; in so far as it may be due to want of that little assistance which the fiscal arrangements in other countries make possible for our rivals, again we are not concerned in this Section; in so far as our patent laws are unique among those of manufacturing nations in allowing the foreigner to manufacture in his own country under the protection of our patent law, so that the most valuable school we possess, the manufactory, as well as the manufacture, is conducted to the advantage of our rivals—a point which I suppose it is unnecessary to commend to the notice of Mr. Chamberlain—with this, too, we have no concern in this Section; but in so far as this, or the want of enterprise or of foresight that leads to it, is due to ignorance and to want of appreciation of scientific advance, we are very much concerned with it. If I may refer to my own limited experience, there is a lamentable contrast in the manner in which a great number of our own countrymen look at any proposition put before them and that in which the alert American does. It is useless to explain that which would be self-evident to a man with a moderate knowledge of chemistry and physics such as our schools ought to supply, or for which they should at least lay the foundation, for the words have no meaning; they are merely words. He distrusts anything new; he has heard of a new process before that did not work out well; experience on the Continent to him is no experience at all, for he believes the inhabitants in such distant parts of the earth are not capable of knowing as well as the enlightened Englishman whether a thing is properly done or not, and so he goes on as he did before, perfectly content. This attitude would not be possible with the most elementary understanding of common principles.

But there is another side to this picture. Anyone who has discussed any scheme with the board of directors, the manager, the engineer, and the chemist of one of our great manufactories must have been struck with the concentrated ability there found in harness. It has often seemed to me that it is a great misfortune that our professors of mechanics, of physics, and of chemistry are in so many instances precluded from a better acquaintance with the working of these great machines—a misfortune not for the works, at least directly, but for the professors, and more especially for their pupils.

Nowhere are scientific problems of greater complexity constantly having to be solved than in a great manufactory; nowhere is such concentrated talent necessary as in a works organised and carried on in competition with all the world. I look upon these as our most valuable schools, and the closer the touch between them and those whose province it is to teach, the better for the teacher and the pupil.

It is, perhaps, hardly desirable to mention any one where there are so many. I am tempted to dwell upon the problem which has been at last successfully solved by Parsons, this being the joint product of the school and of the works; but there is one picture—a contrast, I will not say of light and shade, but of colour and colour—to which I must refer. I remember in my early days, in the surroundings of a classical atmosphere, the general feeling of contempt for the manufacturer, the intellectually inferior creature who only made money, but who knew nothing of τύπτω or τέτυμμαι. I am not sure that some such feeling does not still exist among those whose horizon is limited to the Latin and Greek that they have learned—or should I say limited *by* instead of *to*? This recollection came back to me when not long ago I was visiting one of the best organised and most skilfully conducted works in the country—I mean Willans and Robinson—when I remembered that another great manufactory, conducted on American lines, was near by, and when across the road I saw the walls of one of our most famous English schools. I pictured the old contrast: on the one hand, the conviction impressed upon me when a boy that there is something intellectually superior in the struggle with a paragraph of Xenophon or a page of Homer, while manufacture is merely mechanical, sordid, and base, with what I believe to be the reality on the other. I wondered in what spirit the erection of these works was viewed at the school, and to what extent the high intellectual attainment there so essential and so evident is properly appreciated.

Of the last of the three headings, Strenuousness, we have plenty, but at school it is most apparent in cricket and football, and in after-life in various expensive ways of murdering defenceless animals.

However, a change is already beginning to be felt. The public schools no longer withhold the elements of chemistry and physics, and those who have benefited, even in small degree, are taking responsible places vacated by those who had no such opportunity. The numerous polytechnics are providing more serious instruction to thousands of our young men, and it may be hoped that in time even the official—I mean the mere official whose only conception of activity is centred in obstructing progress and enlightenment—will have some appreciation of things as well as of words.

COSMICAL RADIO-ACTIVITY.*

By ARTHUR SCHUSTER, F.R.S.

The fact that every physical property hitherto discovered in one element has always been found to be shared by all suggests the possibility that radio-activity may be a common property of all matter. If that is the case, the so-called radio-active bodies may only be distinguished from others—like iron in the case of magnetism—by the enormously exaggerated form in which they possess the property. The apparently inactive metals may possess radio-activity, but to so small a degree that our powers of observation are insufficient to detect it. But the question arises whether in that case the effect is cumulative and should appear in the large cosmic aggregations of matter.

There is indeed at first sight some analogy both in the case of the sun and of the earth between the effects observed in their immediate surroundings and those noticed in the neighbourhood of radio-active bodies. The earth we know must be charged with negative electricity, and attention had already for some time been drawn to the fact that this charge must constantly be renewed, as the leakage due to the spraying of ocean waves and the hot gases escaping from every chimney would ultimately dissipate the charge. But the normal electric conductivity of the air has only recently been measured, and, according to Elster and Geitel, is, under normal conditions, such that a body loses about $1\frac{1}{3}$ per cent of its charge per minute. If the air in the immediate neighbourhood of the ground has this conductivity (which is not quite certain) the earth would lose about half its charge in an hour.

We are living therefore—and there can be little doubt about the point—in an electric field through which nega-

* A Paper read before the British Association (Section A), Southport Meeting, 1903.

tively charged particles are constantly driven outwards (cathode rays), and which possess an electric conductivity similar to that found in the neighbourhood of radio-active bodies. The radio-activity of air rising out of the ground or of water drawn out of wells may be the consequence of emanations from a radio-active earth.

The similarity of the rays of the solar corona to cathode rays has often been pointed out, and I have maintained for a long time now that the assumption of a greater conductivity of space at times of maximum sun-spots furnishes a simple explanation of the connection between sun-spots and terrestrial magnetism. The sun therefore, like the earth, must be taken to discharge rays which seem to possess all properties of cathode rays.*

The analogies I have pointed out are not complete, and may be found to be false; but we must, I think, keep our mind open to the possibility of a collective radio-activity of matter which becomes apparent in celestial bodies.

The continuous discharge of negative electricity from the earth renders it necessary to find a cause leading to a continuous renewal, and it is extremely difficult to see what that cause can be.

Though not directly connected with the subject under discussion, I may, in conclusion, digress by recalling an old discussion on the cause of gravity. Lesage's explanation involved the presence of "corpuscles," such as are now believed to exist by some physicists. Maxwell's objection to Lesage's explanation, which at the time seemed fatal, was that gravitation ought to be, but is not, accompanied by a rise in temperature. Whatever we may think of the explanation on other grounds, this particular objection would seem to lose its weight at present, when, in the case of one body at any rate, a rise in temperature above that of its surroundings has actually been discovered, and when it is considered that the energy which in one case accumulates as heat may in other cases be dissipated through other channels.

GRANULAR AND SPICULAR STRUCTURE IN SOLIDS.†

By G. T. BEILBY.

In a communication made to the British Association in 1901 ("Report," 1901, p. 604) I drew attention to certain facts which had apparently escaped the notice of other observers in micro-metallurgy.

It was shown that transparence in metals is not only found in such specially attenuated forms as thin leaves or films deposited on glass, but that it is an intrinsic property of the metal even in its more massive forms. It was further shown that metal surfaces under obliquely-reflected light exhibit a remarkably uniform granular or spicular structure, which appears to be quite distinct from the crystalline structure revealed by the etching methods of micro-metallurgy.

During the past two years my study of this subject has been continued and extended, and some of the results have been already published (*Royal Society Proc.*, vol. lxxii., No. 481).

The object of the present communication is to place on record such confirmation and modification of the original observations and statements as have resulted from the further study of the subject.

The original statements depended on microscopic observations made by obliquely-reflected light with objectives of moderate numerical aperture. This form of illumination can only be conveniently applied with objectives whose working distance is not less than 5 m.m., and whose front lense is not very large. It was therefore desirable that the observations by obliquely-reflected light should be supplemented by others, in which different methods of illumination could be employed.

A study was made of films of metal which were thin enough to transmit light freely. By transmitted light, if such films are not too thin, they show a distinct granular texture, as if the substance had been partly gathered up into minute mounds. By alternatively illuminating one of these films by transmitted and by obliquely-reflected light, it is seen that the structure which is granular by the one light is spicular by the other; the spicular appearance, therefore, is caused by a granular texture. The slightness of this texture is shown by the fact that it is visible by oblique light in metal films which are less than 10 $\mu\mu$ in thickness.

By a parallel study of the surface layer in metals in their more massive forms, it was found that this layer is, in many respects, distinct from the mass which it covers, being in its structure and properties similar to the thin films deposited on glass.

The character of the material on which the film is supported has a considerable influence on the appearance by obliquely-reflected light. In the case of massive metal, the opaque highly-reflecting under-surface adds a light and colour to the spicular appearance, which is absent in that of the thin glass-supported films. But, if due allowance is made for this, the correspondence between the appearance of the two, the surface layer and the thin film, is so exact as to leave no doubt as to the identity of the structure which causes this appearance.

The transparence of thin films of metal was studied by Faraday, and some of his conclusions have been confirmed by subsequent observers. His very remarkable observations on the effect of heat annealing on thin films appear to have dropped out of sight. The subject has been studied by me with the help of lenses of a resolving power much greater than any which could be obtained in Faraday's time. The results of these recent observations confirm and extend Faraday's conclusions, and it is believed that they also supply an answer to certain questions which he raised.

The condition of greatest opacity is found in metal films which are in a state of strain, and the condition of greatest transparence is found in films which have been relieved from strain by annealing. Contrary, therefore, to the generally accepted idea, the metal in gold leaf is in its most opaque condition.

Increase of transparence in metals is accompanied by diminution of reflecting power and *vice versâ*. This effect can be seen most distinctly in translucent films, but it is also quite evident in the surface of the more massive forms of metal. Films of gold and of platinum 200 $\mu\mu$ in thickness have been obtained which are translucent and optically continuous. Films less than 10 $\mu\mu$ in thickness have also been made which appear to be equally continuous, and are perfectly transparent. The thinner films are practically without metallic reflecting power, while even in the thicker films the reflection is distinctly inferior to that of gold leaf.

The process of annealing has been watched on the surface of metal, and the phenomena were found to be similar in kind to those which occur in films supported on glass or mica. In surface films also the increase of transparence was well marked, and the return of the metal to the more lustrous, but less transparent, condition by burnishing was evident.

From the study of the phenomena observed in cutting, polishing, burnishing, and annealing, I have been led to the conclusion that the disturbance caused by these operations temporarily confers a degree of freedom upon the molecules of the surface layer, which enables them to act like a viscous fluid, subject to the influence of the molecular forces as they manifest themselves in surface tension. The dimensions and the forms of the grooves, ridges, and granules on the surface give a general indication that the

* The slight diminution of temperature at times of maximum sun-spots, which seems to be indicated by recent discussion of thermometer readings, may be a result of the increased absorption in space which we must expect to be caused by the presence of a sufficient number of electrons.

† Abstract of a Paper read before the British Association (Section A), Southport Meeting, 1903.

layer affected by this freedom and by the surface tension is many molecules in depth.

It appears probable that the granular structure of the surface is largely a result of surface tension. A similar structure can readily be developed in a very thin film of a viscous fluid. If a little oil is spread on a slip of glass and then almost completely wiped off, so that it is barely visible to the unaided eye, a granular film is produced which gives a well-marked spicular appearance by obliquely-reflected light. A film of varnish on a non-reflecting support shows the same structure. A thin film of fuchsin on glass shows a structure and a play of colour which might almost be mistaken for that of a feebly-reflecting gold film. Films of oxide or sulphide on metal surfaces show the spicular appearance very brilliantly.

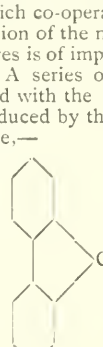
This surface granulation appears to be almost universal, and I have never failed to produce it in any solid with which I have experimented.

Granular or spicular structure seems to be closely associated with the deposition of solids from solution. It is seen in thin films of metal deposited either chemically or electrolytically. In precipitates formed in very dilute solutions there are three stages in the appearance of the solid:—(1) Spicules or spicular films of extreme thinness, (2) granules, and (3) crystals. Spicules may be formed singly, but they often result from the breaking up of the thin films which are formed at the surface of contact of the two reagents. Their pedetic movements lead to their agglomeration into granules, which sink to the bottom of the containing vessel, where they become centres of attraction to the moving spicules and grow by their absorption. Till the granule has reached a certain size and mass it shows no indication of crystalline form or structure, and its form remains, under the control of surface tension, rounded and granular. When a certain size is reached, the crystallic force begins to assert itself and to overpower surface tension, and the rounded form begins to develope faces and angles till, finally, a well-developed crystal is produced.

ON SOME DERIVATIVES OF FLUORENE.*

By Miss IDA SMEDLEY.

Assuming, as Professor Armstrong has contended, that all visibly coloured substances contain three separate light-absorbing centres which co-operate in producing the colour effect, the determination of the nature of the radicles which can act as such centres is of importance (compare "Encyc. Brit.," xxvi., 745). A series of fluorene derivatives has therefore been studied with the object of ascertaining the change in colour produced by the introduction of different radicles. Fluorenone,—



being a coloured ketone, was chosen as the starting-point from which to prepare compounds containing the radicles $>CCl_2$, $>CS$, in place of the carbonyl group.

The chloride prepared by the action of phosphorus pentachloride on fluorenone is a colourless compound. In the derivatives of hydrindonaphthene and of naphthalene prepared by Zincke (*Ber.*, xx., 2053; xxi., 3540), the displacement of the carbonyl group by the group $>CCl_2$ is also attended by a loss of colour. It would appear, therefore, that the radicle $>CCl_2$ does not function as a "colour-centre."

Thiofluorenone was prepared by the action of K_2S on fluorenone chloride. The substitution of the thio-carbonyl for the carbonyl group is accompanied by an increase in colour, an intense red compound being formed instead of the orange-yellow fluorenone. The colour of the thioketones is of special interest, since thiobenzophenone and the substituted thio-benzophenones are deep blue, and all give violet solutions (*Ber.*, xxviii., 2869). The co-operation of the thio-carbonyl group with other centres is necessary, since, in compounds such as thiourea the presence of this group alone is insufficient to condition colour. The greater tendency of the radicle $>CS$ to produce colour, when compared with the carbonyl group, is probably connected with its more unsaturated character as shown by the ease with which disulphides are formed. The disulphide of fluorene has been prepared, and like other known disulphides is colourless.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

ACTION OF DIASTASE ON THE STARCH GRANULES OF RAW AND MALTED BARLEY.*

By ARTHUR R. LING.

The whole of the published data referring to the hydrolysis of starch by diastase have been derived from the study of the action of the enzyme on potato-starch paste, and the application of these to practical purposes has led to misleading and erroneous conclusions. The starches of barley and other cereals differ from that of the potato in being readily attacked by a solution of diastase in the ungelatinised condition.

The author has carried out a series of mashes with barley and malt starch of various origin, the starch being mixed with the diastase preparation in the dry state and mashed with water at different temperatures for two hours.

The following table illustrates the results obtained:—

Starch employed.	Mashing temperature.	$[\alpha]_{D\ 3\cdot93}$.	$^*R_{3\cdot93}$.
	°	°	
Barley, 1899 sample ..	60	140·8	88·7
,, ,, ,, ..	65·5	143·4	88·2
,, ,, ,, ..	71	145·1	80·6
,, 1902 sample ..	60	150·7	84·2
,, ,, ,, ..	65·5	152·3	79·0
,, ,, ,, ..	71	163·8	77·8
Kilned malt	60	150·9	84·4
,, ,, ...	65·5	156·1	80·6
,, ,, ...	71	161·3	67·2
Low-dried malt	60	151·6	85·3
,, ,, ...	65·5	152·5	83·3
,, ,, ...	71	165·7	66·6
Barley-starch (paste) ..	65·5	168·6	52·4
Potato-starch (paste) ..	60	154·5	81·8
,, ,, ..	65·5	155·6	71·5
,, ,, ..	71	167·1	55·3

* The symbol R denotes the percentage of apparent maltose, determined by the cupric reduction method, on the dissolved matter in solution. The symbols $[\alpha]_{D\ 3\cdot93}$ and $R_{3\cdot93}$ indicate that the total solids have been calculated from the specific gravity of the solution by the divisor 3·93.

The very great differences between the constants yielded by the starch mashes and the starch paste conversions are apparent. It is also to be noted that the starches from different barleys give different constants, and the author hopes to continue his work in this direction. He brings forward evidence showing that in the process of mashing, as conducted in breweries, the starch granules are dissolved directly by the diastase and are not gelatinised prior to hydrolysis, as it is usually stated they are. It is probable

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

that the products formed in these starch mashes are different from those resulting from the hydrolysis of starch paste; and it is hoped that a study of the former may yield results of importance, both theoretically and practically.

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 160).

Chapter III.

Radiation of the New Radio-active Substances.

Methods of Investigation of the Radiation.

In order to investigate the radiation emitted by radio-active bodies, any one of the properties of this radiation can be utilised. Thus the action of the rays on photographic plates may serve, or their property of ionisation of the air, which renders it a conductor, or their capacity for causing fluorescence of certain bodies. Henceforth, in speaking of these different methods of working, I shall use the expressions radiographic method, electrical method, fluoroscopic method.

The first two have been used from the beginning in the study of uranium rays; the fluoroscopic method can only be applied in the case of the new bodies which are strongly radio-active, for the feebly active bodies such as uranium and thorium produce no appreciable fluorescence. The electrical method is the only one which serves for exact determinations of intensity; the other two are specially adapted for giving qualitative results, and only furnish rough approximations The results obtained with the three methods just considered are not strictly comparable the one with the other. The sensitive plate, the gas which is ionised, the fluorescent screen, are in reality receivers, which absorb the energy of the radiation, and transform it into another kind of energy, chemical energy, ionic energy, or luminous energy. Each receiver absorbs a fraction of the radiation, which depends essentially upon its nature. Later on, we shall see that the radiation is complex, that the fractions of the radiation absorbed by the different receivers may differ among themselves both quantitatively and qualitatively. Finally, it is neither evident, nor even probable, that the energy absorbed is entirely transformed by the receiver into the form that we wish for observation; part of this energy may be transformed into heat, into the evolution of secondary radiations which may or may not assist in the production of the observed phenomenon, into chemical action which differs from that under observation, &c., and here also the effective action of the receiver, with reference to the end we have in view, depends essentially upon the nature of that receiver.

Let us compare two radio-active substances, one containing radium and the other polonium, and which show an equal degree of activity in the condenser of Fig. 1. If each is covered with a thin leaf of aluminium, the second appears considerably less active than the first, and the same is the case when they are placed under the same fluorescent screen, if the latter is of sufficient thickness, or is placed at a certain distance from the two radio-active bodies.

Energy of Radiation.

Whatever be the method of research employed, the energy of radiation of the new radio-active substances is always found to be considerably greater than that of uranium and thorium. Thus it is that, at a short distance, they act instantaneously upon a photographic plate, whereas an exposure of twenty-four hours is necessary when operating with uranium and thorium. A fluorescent screen is vividly illuminated by contact with the new radio-active bodies, whilst no trace of luminosity is visible with uranium and thorium. Finally, the ionising action upon air is considerably stronger in the ratio of 10^4 approximately.

* Thesis presented to the Faculté des Sciences de Paris

But it is, strictly speaking, not possible to estimate the *total intensity of the radiation*, as in the case of uranium, by the electrical method described at the beginning (Fig. 1). With uranium, for example, the radiation is almost completely absorbed by the layer of air between the plates, and the limiting current is reached at a tension of 100 volts. But the case is different for strongly radio-active bodies. One portion of the radiation of radium consists of very penetrating rays, which penetrate the condenser and the metallic plates, and are not utilised in ionising the air between the plates. Further, the limiting current cannot always be obtained for the tensions supplied; for example, with very active polonium the current remains proportional to the tension between 100 and 500 volts. Therefore the experimental conditions which give a simple interpretation are not realised, and, consequently, the numbers obtained cannot be taken as representing the measurement of the total radiation; they merely point to a rough approximation.

Complex Nature of the Radiation.

The researches of various physicists (MM. Becquerel, Meyer and von Schweidler, Giesel, Villard, Rutherford, M. and Mdme. Curie) have proved the complex nature of the radiation of radio-active bodies. It will be convenient to specify three kinds of rays, which I shall denote, according to the notation adopted by Mr. Rutherford, by the letters α, β, γ.

I. The α-rays are very slightly penetrating, and appear to constitute the principal part of the radiation. These rays are characterised by the laws by which they are absorbed by matter. The magnetic field acts very slightly upon them, and they were formerly thought to be quite unaffected by the action of this field. However, in a strong magnetic field, the α-rays are slightly deflected; the deflection is caused in the same manner as with cathode rays, but the direction of the deflection is reversed; it is the same as for the canal rays of the Crookes tubes.

II. The β-rays are less absorbable as a whole than the preceding ones. They are deflected by a magnetic field in the same manner and direction as cathode rays.

III. The γ-rays are penetrating rays, unaffected by the magnetic field, and comparable to Röntgen rays.

Consider the following imaginary experiment:—Some radium, R, is placed at the bottom of a small deep cavity, hollowed in a block of lead, P (Fig. 4). A sheaf of rays,

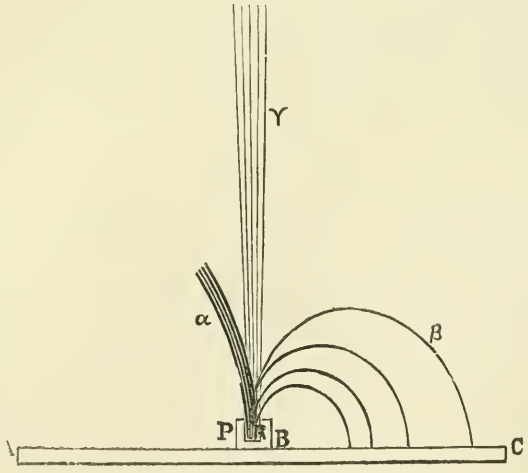


Fig. 4.

rectilinear and slightly expanded, streams from the receptacle. Let us suppose that a strong uniform magnetic field is established in the neighbourhood of the receptacle, normal to the plane of the figure and directed towards the back. The three groups of rays, α, β, γ, will now be separated,

Then rather faint γ-rays continue in their straight path without a trace of deviation. The β-rays are deflected in the manner of cathode rays, and describe circular paths in the plane of the figure. If the receptacle is placed on a photographic plate, A C, the portion, B C, of the plate which receives the β-rays is acted upon. Lastly, the α-rays form a very intense shaft which is slightly deflected, and which is soon absorbed by the air. These rays describe in the plane of the figure a path of great curvature, the direction of the deflection being the reverse of that with the β-rays.

If the receptacle is covered with a thin sheet of aluminium (0·1 m.m. thick), the α-rays are suppressed almost entirely, the β-rays are lessened, and the γ-rays do not appear to be absorbed to any great extent.

Action of the Magnetic Field.

We have seen that the rays emitted by radio-active bodies have many properties common to cathode rays and to Röntgen rays. Cathode rays, as well as Röntgen rays, ionise the air, act on photographic plates, cause fluorescence, undergo no regular reflection. But the cathode rays differ from Röntgen rays in being deflected from their rectilinear path by the action of the magnetic field, and in the transportation of charges of negative electricity.

The fact that the magnetic field acts upon the rays emitted by radio-active substances was discovered almost simultaneously by MM. Giesel, Meyer and von Schweidler, and Becquerel. These physicists observed that the rays of radio-active substances are deflected by the magnetic field in the same manner and direction as the cathode rays; their observations were in relation to the β-rays.

M. Curie demonstrated that the radiation of radium comprises two groups of quite distinct rays, of which one is readily deflected by the magnetic field (β-rays), whilst the other seems to be unaffected by the action of this field (α- and γ-rays).

M. Becquerel did not find that the specimens of polonium prepared by us emitted rays of the cathode kind. On the contrary, he first noticed the effect of the magnetic field on a specimen of polonium prepared by himself. None of the polonium prepared by us ever gave rise to rays of the cathode order.

The polonium of M. Giesel only gives rise to these rays when recently prepared, and it is probable that the emission is due to the phenomenon of induced radio-activity of which we shall speak later.

The following are experiments which prove that one portion of the radiation of radium, and one portion only, consists of easily deflected rays (β-rays). These experiments were done according to the electrical method.

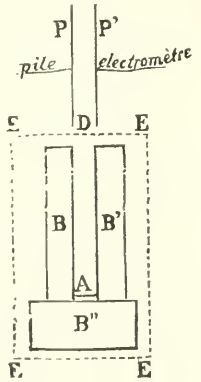


Fig. 5.

The radio-active body A (Fig. 5) sends forth radiations in the direction A D between the plates P and P'. The plate P is now at a potential of 500 volts, plate P' is connected to an electrometer and to a quartz electric piezometer. The intensity of the current passing through the air under the influence of the radiations is measured. The magnetic field can be established at will perpendicular to the plane of the figure over the whole region E E E E. If the rays are deflected, even slightly, they no longer pass between the plates, and the current is suppressed. The region of the passage of the rays is surrounded with masses of lead, B, B', B'', and by the armatures of the electro-magnet; when the rays are deflected, they are absorbed by the masses of lead B and B.

The results obtained depend essentially on the distance, A D, of the radiating substance, A, from the condenser at D. If the distance A D is great enough (greater than 7 c.m.), most of the radium rays (90 to 100 per cent) arriving at the condenser are deflected and suppressed for a field of 2500 units. These are the β-rays. If the distance A D is less than 65 m.m., a smaller part of the rays are deflected by the action of the field; this portion is also entirely deflected by a field of 2500 units, and the proportion of the rays suppressed is not increased by increasing the field from 2500 to 7000 units.

The proportion of the rays not suppressed by the field increases with decrease of the distance, A D, between the radiating body and the condenser. For small distances, the rays which can be easily deflected form a very small fraction of the total radiation. The penetrating rays are therefore, for the most part, deviable rays of the cathode order (β-rays).

Under the experimental conditions just described, the action of the magnetic field on the α rays could not be well observed for the fields employed. The chief radiation, apparently undergoing no deflection, observed at a short distance from the radiating source, consisted of α-rays; the undeflected radiation observed at a greater distance consisted of γ-rays.

If an absorbing lamina (aluminium or black paper) is placed in the path of the bundle of rays, those which pass through are nearly all deflected by the field in such a way that, with the aid of the screen and the magnetic field, almost all the radiation is suppressed in the condenser, the remainder being due to the γ-rays, the proportion of which is small. The α-rays are absorbed by the screen.

An aluminium plate of $\frac{1}{10}$ m.m. thickness is sufficient for the suppression of almost all the rays not readily deflected when the substance is far enough from the condenser; for smaller distances (34 m.m. and 51 m.m.) two pieces of this aluminium foil are necessary to give the same result.

Similar determinations were made with four substances containing radium (chlorides or carbonates) of very different activity; analogous results were obtained.

It may be remarked that, in all cases, the penetrating rays deflected by the magnet (β-rays) form only a small fraction of the total radiation; they influence but slightly the determinations in which the whole radiation is made use of to produce conductivity of the air.

The radiation emitted by polonium may be studied by the electrical method. When the distance, A D, of the polonium from the condenser is varied, no current is observed at first while the distance is fairly great; on nearing the polonium, the radiation suddenly becomes manifest with great intensity; the current then increases uniformly whilst approaching the polonium, but the magnetic field produces no appreciable effect under these conditions. The radiation of polonium is apparently limited in space, and does not pass into the air beyond a kind of sheath surrounding the substance to a thickness of several centimetres.

The interpretation of the experiments I have just described must be accompanied by some important general reservations. In speaking of the proportion of the rays deflected by the magnet, I refer only to that portion of the radiation capable of causing a current in the condenser. In employing the fluorescent action of the Becquerel rays, or their action on photographic plates, the proportion would probably be different—a measure of intensity having, as a rule, no meaning except for the method of measurement adopted.

The rays of polonium are α-rays. In the experiments just described, I observed no action of the magnetic field upon them, but the experimental conditions were such that a slight deflection would pass unnoticed.

The experiments made by the radiographic method confirmed the preceding results. Taking radium as the source of radiation, and receiving the impression on a plate parallel to the primitive shaft and normal to the field, a very clear print is obtained of two shafts separated by the action of the field, the one deflected, the other not deflected. The β-rays constitute the deflected beam; the α-rays, being very slightly deflected, are not to be distinguished from the undeflected bundle of the γ-rays.

(To be continued).

NOTES ON THE COMPOSITION OF SOME ANCIENT SLAG.

By A. W. COMBER, A.I.C., F.C.S.

A year or two ago, when on the Island of Elba—famed for its iron ores as well as its Napoleonic associations—I was asked to make some analyses of samples of ancient slag.

That the Elban ore was worked by the Romans, and probably by the Greeks, is a well-assured fact, borne out by more than one reference in the classics, and the slag in question, of which considerable quantities are found on the island, exists to-day as an interesting evidence of those early metallurgical operations.

I made two analyses of this slag, the results of which are herewith appended. The first sample (*a*) consisted of only one piece, while of (*b*) I was supplied with a considerable quantity, and, consequently, the latter should be taken as more truly representative of the general constitution of the slag.

	(*a*).	(*b*).
Silica	16·27	25·95
Ferric oxide (Fe_2O_3)	15·23	15·86
Ferrous oxide (FeO)	56·24	44·67
Oxide of aluminium	5·81	7·31
Oxide of manganese	0·47	0·40
Oxide of calcium	2·37	2·00
Oxide of magnesium	0·77	0·67
Phosphoric acid (P_2O_5)	0·156	0·232
Sulphuric acid (SO_3)	0·072	0·120
Arsenic acid (As_2O_5)	nil	nil
Water above 100° C.	1·70	1·80
Water at 100° C.	0·88	0·98
	99·968	99·992
	Per cent.	Per cent.
Metallic iron	54·41	45·84
Phosphorus	0·068	0·102
Sulphur	0·029	0·047

The results, apart from the high percentage of iron and the somewhat large quantity of phosphorus, do not call for special comment.

In considering the apparent waste of iron, it should be remembered, however, that apart from their extremely primitive plant, these ancient workers, by reason of the small quantity of ore operated upon, were able to carefully select their material, utilising only such pieces of ore as were apparently of the highest grade.

To illustrate this, I give an analysis of a selected sample of Elban ore which I made a few months previously:—

	Ore dried at 100° C.
	Per cent.
Iron	68·89
Phosphorus	trace
Sulphur	nil
Silica	trace

This of course hardly explains the high phosphorus result in the slag, which, however, may have been caused by other means, but it is sufficient to indicate that, if judiciously selected, ore of exceptionally high quality was at hand to be utilised. I might here mention that during my stay in Elba the ore exported averaged considerably over 60 per cent of iron, the analyses being made on samples dried at 100° C.

Assuming, therefore, the ore taken for smelting to have contained 65 per cent of iron, one can readily see that a fair margin for extraction is left, even when the metal remaining amounts to nearly one-half of the slag, especially if one considers the matter from the standpoint of the old-time metallurgist to whom time was no object, neither was he so circumstanced that the cost of production had to be calculated out to the fraction of a denarius!

Ramabudrapur, India.

NOTICES OF BOOKS

Practical Electro-Chemistry. By Bertram Blount, F.I.C., F.C.S., Assoc.Inst.C.E. Second Impression. Westminster: Archibald Constable and Co., Ltd. New York: The Macmillan Company. 1903.

The title of this book, the success of which has been great enough to warrant the production of a second impression, is perhaps somewhat misleading; it does not contain descriptions of experiments with directions for their performance, but gives an account of the practice of electro-chemistry as applied to manufacture and commercial processes. The subjects dealt with include the winning and refining of metals and their alloys by electrolytic methods, electro-deposition, and the manufacture of organic compounds and fine chemicals. The author has very wisely omitted historical matter, which has by no means diminished the value of the book for all practical purposes, while increasing the space available for the consideration of details as to expense and cost of working; the three years which have elapsed since the first appearance of the book have in many cases considerably affected the magnitude of these values, which were perhaps sometimes rather over estimated originally, as in the case of aluminium, but on the whole the statements will be found trustworthy. A few comparatively unimportant misprints are scattered through the book, and some omissions are noticeable; for example, no mention is made of the preparation of the metals of the alkaline earths by the electrolysis of the fused chlorides which has been effected by a special process said to be applicable on a large scale. But on the whole the treatment of the subject is most practical and efficient, and the book will be found quite indispensable by the student of electro-chemistry.

Elektro-metallurgie des Nickels. ("The Electro-metallurgy of Nickel"). By Dr. W. Borchers. Halle-a-S.: Wilhelm Knapp. 1903,

The details of the processes of nickel refining and plating as actually employed commercially are very little known, though great activity has been displayed by many workers in the investigation of the chemical and physical facts which underlie their successful performance. This monograph therefore, while it does not reveal the special methods adopted by the largest and most important firms, does much to supply a want in collecting and editing the copious accounts of researches of the electro-chemical treatment of crude nickel, and abstracting patent specifications. As a compilation of this sort it will be found an excellent example of judicious selection, though perhaps a rather undue prominence is given to the description of old methods which, although interesting from the point of view of the development of present processes, have long since ceased to be of any practical value whatever. The author

deals first with the treatment of crude cast nickel without reference to the separation of the metal from copper, and then proceeds to the special means of obtaining chemically pure nickel, and the processes used for the electrolytic deposition of the metal. Mond's method of volatilisation and decomposition of nickel carbonyl is dismissed with a very brief description, amounting to a few lines only.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxix., No. 7.

Separation and Estimation of Antimony by Electrolysis.—A. Hollard.—Already inserted in full.

Separation and Estimation of Zinc by Electrolysis.—A. Hollard.—Already inserted in full.

Sulphurised and Azotised Derivatives of Sulphide of Carbon. (X.). Thermochemistry.—Marcel Delépine.—The author burnt, in a Berthelot calorimetric bomb, some of the principal substances used in his research on the sulphurised and azotised derivatives of sulphide of carbon, as well as some others belonging to another order, but having some isomeric relations with them. The results obtained are given in a table, and some interesting conclusions may be drawn therefrom.

The Nitration of Furfurane. (I.).—R. Marquis.—The author has effected the nitration of furfurane in solution in acetic anhydride. Under these conditions he did not immediately obtain nitrofurfurane, but a special reaction took place which caused the break-up of the furfuranic radical and the formation of a derivative of succinic aldehyde. This liquid, nitrated derivative, insoluble in water, is remarkably unstable; it decomposes, sometimes spontaneously, giving off nitrous fumes and leaving a voluminous residue of carbon. Two special reactions have enabled the author to establish its constitution. Decomposition by means of water gives rise to the formation of nitrous acid, acetic acid, and fumaric aldehyde. The formation of fumaric aldehyde is again shown by another reaction. When the derived nitrated liquid is treated with hydrazine, orthodiazine can be isolated from the product of the reaction. Now this base may be considered as the aldazine of fumaric aldehyde. The preceding reactions give to this nitrated derivative the constitution of an acetylised derivative of nitrosuccinic aldehyde, with the formula—

$$\begin{array}{l} NO_2—CH—CHO \\ \quad | \\ \quad CH=CHO—COCH_3 \end{array}.$$

The Nitration of Furfurane. (II.). β-Nitrofurfurane and Dinitrofurfurane.—R. Marquis.—After some experiments the author adopted the following method for the nitration of furfurane:—For 1 part of furfurane he used 5 parts of fuming nitric acid added drop by drop, and 8 parts of acetic anhydride cooled in ice and salt. When all the furfurane has been added, the mixture is thrown on to broken ice, and exhausted three or four times with ether. The ethereal solution is washed with a solution of bicarbonate of soda until no longer acid, then with water. The solution is then dried over anhydrous sulphate of soda, and distilled on the water-bath until about three-quarters of the ether is driven off; the remainder is removed *in vacuo* in the cold. The residue, which is a thick yellow liquid, insoluble in water, is nitrosuccinic acetine. This liquid is treated with pyridine, and the excess distilled off *in vacuo* on the water-bath. The residue is carried over by the steam, and an oily liquid appears in the condenser; it solidifies in the flask, and consists of the nitro-furfurane sought for. This nitrofurfurane is purified by crystallisation in petroleum ether, and when treated with boiling nitric acid of 1·2 density, it is transformed into a dinitrated derivative. This substance is identical with the dinitrofurfurane obtained by Messrs Hill and White (*Am. Chem. Journ.*, vol. x., p. 380), by treating sulphopyromucic acid with nitric acid.

Estimation of Vanilline in Vanillas.—A. Moulin.—While working on the colorimetric estimation of dulcine, the author came across an intense colouration which was recognised as being due to the presence of vanilline. The vanilline was eliminated by means of an excess of bisulphite of sodium, and an attempt made to apply the colorimetric method to the estimation of this substance. The principle of the method adopted was as follows:—If vanilline, $C_6H_3\begin{cases} OCH_3 \\ OH \\ CHO \end{cases}$, in which the group $C_6H_3—O—CH_3$ is found, is treated with fuming nitric acid, this group passes to the state of picrate of methyl, the solution of which is characterised by the yellow tint of the picric compounds, and serves for the estimation of the vanilline by comparison with a titrated colour scale.

Method of Estimating Glycerin in Wine.—A. Trillat.—Already noticed.

The Entanglement of Glycerin by Water-vapour. Maurice Nicloux.—The distillation of glycerin by means of steam, either *in vacuo* or superheated, offers several disadvantages. The author has devised a new apparatus for this distillation, and describes it fully. The following are some of the results obtained:—

Glycerin used. M.grm.	Volume of liquid carried over. C.c.	Glycerin recovered. M.grm.
10·2	120	9·8
25·6	180	25·5
43·0	260	44·1
76·9	320	76·0
102·5	514	101·0

Composition of Sheep's Milk.—MM. Trillat and Forestier.—Analyses were made of 171 samples of sheep's milk, of which 37 are given here in full. The extract was taken by evaporating 10 c.c. of the milk for seven hours on the water-bath, in a platinum crucible 7 c.m. in diameter. The sugar was estimated on 10 c.c. of liquid; the lactose was titrated by Fehling's solution. The butter was obtained by treating the coagulum with ether, and weighing the portion extracted; the casein was estimated by difference. The figures given are somewhat higher than those found by other analysts. It is interesting to observe that the weight of the extract is often as high as 200 grms. per litre of sheep's milk, while in the case of cow's milk it is rarely more than 150 to 160 grms. The ash, generally about 9 grms., shows that sheep's milk is more highly mineralised than cow's milk.

MISCELLANEOUS.

Announcement.—Messrs. Gurney and Jackson will issue before the end of October Volume I., containing Parts I. and II., of the third and greatly enlarged edition of Dr. George Lunge's "Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali."

The Action of Organic Acids on Metallic Antimony.—B. Moritz and C. Schneider.—Observation has shown that finely divided metallic antimony is soluble in the presence of air, in aqueous solutions of certain organic acids, and of their acid salts. The authors establish first of all, by measurements made with solutions of citric or lactic acid partially saturated with carbonate of soda, the essential *rôle* played by the oxygen of the air; solution does not take place in an inert atmosphere. The amount of oxygen absorbed for each atom of antimony dissolved corresponds to the formation of the oxide, Sb_2O_3. The amount of antimony dissolved, in the presence of an excess of air, increases first with the amount of alkaline carbonate

introduced into the solution, reaches a maximum, and then decreases if we continue to add more carbonate of soda. The amount corresponding to the maximum action is lower than that which would be necessary for the formation of a neutral salt of sodium and antimonyl. The authors then looked for the organic acids capable of dissolving antimony under these conditions. The simple acids of the fatty series, saturated or non-saturated, are without action. On the other hand, the monobasic acid alcohols (glycolic, lactic, α-oxybutyric, β-oxybutyric, oxyisobutyric), give rise to the phenomena in a most distinct manner. It is the same with oxalic acid, but not with malonic, succinic, malic, tartaric, and citric. Thus we see that the property of dissolving antimony in the presence of air is almost entirely limited to the acid alcohols.—*Zeit. Physik. Ch.*, vol. xli., p. 129.

Reaction between Persulphate of Potasslum and Hydriodic and Phosphorous Acids; an Example of Catalysis by Transport.—Wilhelm Federlin.—Persulphate of potassium only oxidises phosphorous acid very slowly, while it rapidly transforms hydriodic acid into iodine; on the other hand, iodine rapidly oxidises phosphorous acid. The addition of hydriodic acid to a mixture of persulphate and phosphorous acid thus accelerates the reaction of these two bodies one on the other; in this manner, the hydriodic acid would play the part, in this reaction, of a catalyser by transport. The examination made by the author of the total speed of the reaction, as well as of those of the two simple reactions, of which it is the result, shows that if we put on one side the interference caused by the presence of PO_3H_3 in the reaction of $S_2O_8K_2$ on KI, and also take note of the incorrectness of the mathematical formula used, there is sufficient concordance between the speed observed and the speed calculated from the speeds of the component reactions. These latter therefore have not any particular influence on each other. Iron and copper, which accelerate the reaction of $S_2O_8K_2$ on KI, have a more feeble catalytic action in the presence of PO_3H_3, perhaps because they are fixed by this acid, or by the phosphoric acid resulting from its oxidation.—*Zeit. Physik. Ch.*, vol. xli., p. 565.

Molybdic Acid.—F. Mylius.—There is no hydrate of molybdic acid corresponding to orthotelluric acid, $Te(OH)6$, the white milky precipitates of molybdic acid are badly defined. The colourless molybdic acid in aqueous solution corresponds in its properties generally with allotelluric acid. On the other hand, there is a yellow molybdic acid, $(MoO_5H_4)x$, which is formed slowly by the action of nitric or hydrochloric acid on solutions of the alkaline molybdates, or of white molybdic acid. An acid molybdate of ammonium, $NH_3,4MoO_3,6H_2O$, has been prepared which, on being heated, first loses half its ammonia and its water; if heated more strongly, the residue becomes green as a result of reduction. This salt is deposited in small colourless needles by the addition of NO_3H, HCl, or SO_4H_2 in quantities calculated from the solution of ordinary molybdate of ammonia; the white cheesy molybdic acid is first formed, and this becomes gradually changed. This salt is slightly soluble in cold water, easily soluble in hot water, but at about 60° the solution changes, giving a deposit of a less hydrated insoluble salt. It has a very acid reaction, and decomposes the carbonates. It precipitates albumin; its solution is not precipitated immediately by nitric acid; eventually it forms still more acid salts, or the yellow acid. The author further announces the existence of the following salts:—

$$Mo_4O_{13}Na_2+6H_2O\ ;\ Mo_4O_{13}NaH+8H_2O\ ;$$
$$Mo_4O_{13}KH+6H_2O\ ;\ Mo_4O_{12}NH_3+6H_2O.$$

—*Berichte*, vol. xxxvi., p. 638.

Sesquisulphide of Phosphorus.—J. Mai and F. Schaffer.—With the object of examining some of the properties of, and the conditions under which commercial sesquisulphide of phosphorus, used for the manufacture of matches, undergoes change, the authors heated some of this substance to 180° for some hours in a current of carbonic acid; a little phosphoretted hydrogen was given off (resulting from a trace of PO_3H_3), as well as fumes, luminous in the dark, and a slight yellow sublimate; these two latter occurrences are due to the distillation of P_2S_3. If we commence with P_2S_3, re-crystallised in sulphide of carbon or in a hydrocarburised solvent, the same phenomena occur, with the exception of the formation of the phosphoretted hydrogen. When heated in the air for some time at about 40—50° the P_2S_3 changes by slow oxidation, becomes luminous in the dark, and is converted into a pitchy mass with a strongly acid reaction. When heated in a current of steam, the P_2S_3 is carried off, giving a white deposit formed principally of P_2S_3, with products of its oxidation. The fumes are luminous in the dark, like phosphorus in Mitscherlich's experiment; however, to a trained eve the phosphorescent appearance is slightly different. Finally, above 350°, in a current of carbonic acid, the P_2S_3 changes rapidly, furnishing considerable quantities of red phosphorus.—*Berichte*, vol. xxxvi., p. 870.

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2289.

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 171).

Chapter III. (*continued*).

Deflected β-Rays.

The experiments of M. Giesel and MM. Meyer and von Schweidler showed that the radiation of the radio-active bodies is in part, at least, deflected by a magnetic field, and that this deflection resembles that of the cathode rays. M. Becquerel investigated the action of the field on the rays by the radiographic method. The experimental arrangement was that of Fig. 4. The radium was placed in the lead receptacle P, and this receptacle was placed on the sensitive face of a photographic plate, A C, covered with

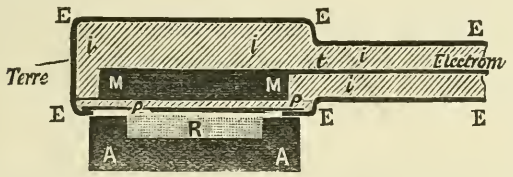


Fig. 6.

black paper. The whole was placed between the poles of an electro-magnet, the magnetic field being normal to the plane of the figure.

If the field is directed to the back of this plane, the part, B C, of the plate is acted upon by rays which, after having described circular paths, return to the plate and strike it at a right angle. These rays are β-rays.

M. Becquerel has demonstrated that the impression consists of a wide diffused band, a continuous spectrum indeed, showing that the sheaf of deviable rays emitted by the source is formed of an infinite number of radiations unequally deflected. If the gelatin of the plate be covered with different absorbent screens (paper, glass, metals), one portion of the spectrum is suppressed, and it is found that the rays most deflected by the magnetic field—otherwise those which have the smallest radius of curvature—are the most completely absorbed. With each screen, the impression on the plate begins at a certain distance from the source of radiation, this distance being proportional to the absorptive power of the screen.

Charge of the Deflected Rays.

The cathode rays are, as shown by M. Perrin, charged with negative electricity. Further, according to the experiments of M. Perrin and M. Lenard, they are capable of carrying their charge through the metallic envelopes connected to earth and through isolating screens. At every point where the cathode rays are absorbed, there is a continuous evolution of negative electricity. We have proved that the same is the case for the deflected β-rays of radium. *The deviable β-rays of radium are charged with negative electricity.*

(Note.—Let the radio-active substance be placed on one of the plates of a condenser, this plate being connected to earth; the second plate is connected to an electrometer, it receives and absorbs the rays emitted by the substance. If the rays are charged, a continuous flow of electricity into the electrometer should be observed. In this experiment, carried out in air, we were not able to detect a charge accompanying the rays, but such an experiment is not delicate. The air between the plates being caused by the rays to conduct, the electrometer is no longer isolated, and can only respond to charges if these be sufficiently strong. In order that the α-rays may not interfere with the experiment, they may be suppressed by covering the source of radiation with a thin metallic screen. We repeated this experiment, without more success, by causing the rays to pass through the interior of a Faraday cylinder in connection with the electrometer).

According to the preceding experiments, it was evident that the charge of the rays of the radiating body employed was a weak one.

In order to fix a feeble evolution of electricity upon the conductor which absorbs the rays, this conductor should be completely insulated; this is effected by screening it from the air, either by placing it in a tube with a very perfect vacuum, or by surrounding it with a good solid dielectric. We employed the latter arrangement.

A conducting disc, M M (Fig. 6), is connected by the wire, *t*, to the electrometer; the disc and wire are completely enveloped by the insulating substance *iiii*; the whole is again surrounded with the metallic covering, E E E E, which is in electric connection with the earth. The insulator, *p p*, and the metallic envelope are very thin upon one of the faces of the disc. This face is exposed to the radiation of the barium and radium salt, R, placed outside

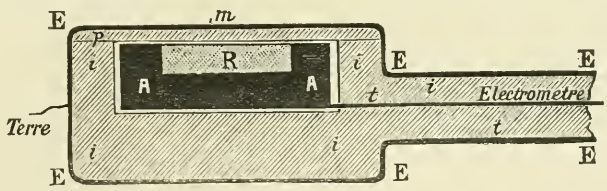


Fig. 7.

in a lead receptacle. The rays emitted by the radium penetrate the metallic envelope and the insulating lamina, *p p*, and are absorbed by the metallic disc, M M. The latter then becomes the source of a continuous evolution of negative electricity, as determined by the electrometer, and is measured by means of a quartz piezometer.

The current thus created is very weak. With very active barium-radium chloride, forming a layer of 2·5 sq. c.m. in area, and of 0·2 c.m. in thickness, a current of magnitude 10^{-11} ampères is obtained, the rays utilised having traversed, before being absorbed by the disc M M, a thickness of aluminium of 0·01 m.m., and a thickness of ebonite of 0·3 m.m.

We used successively lead, copper, and zinc for the disc MM, ebonite and paraffin for the insulator; the results obtained were the same.

The current diminishes with increasing distance from the source of radiation, R, also when a less active product is used.

We obtained the same results again when the disc M M is replaced by a Faraday cylinder filled with air, and covered outside with insulating material. The opening of the

* Thesis presented to the Faculté des Sciences de Paris.

cylinder, closed by the thin insulating plate, *p p*, was opposite the radiating source.

Finally, we made the inverse experiment, which was to place the lead receptacle with the radium in the centre of the insulating material and in connection with the electrometer (Fig. 7), the whole being surrounded with the metallic covering connected to earth.

Under these conditions, it is evident from the electrometer that the radium has a positive charge equal in magnitude to the negative charge of the former experiment. The radium rays penetrate the thin dielectric plate, *p p*, and leave the conductor inside carrying with them negative electricity.

The α-rays of radium do not interfere in these experiments, being almost completely absorbed by a very thin layer of matter. The method just described is not suitable for the study of the charge of the rays of polonium, these rays very slightly penetrating. We observed no indication of any charge in the case of polonium, which gives rise to α-rays only; but, for the reason just given, no conclusion can be drawn from this.

Thus, in the case of the deflected β-rays of radium, as in the case of cathode rays, the rays carry a charge of electricity. But, hitherto, the existence of electric charges uncombined with matter has been unknown. In the study of the emission of the β-rays of radium, we are therefore led to make use of the theory which is in vogue for the study of cathode rays. In this ballistic theory, formulated by Sir William Crookes, since developed and completed by Prof. J. J. Thomson, the cathode rays consist of extremely minute particles, which are hurled from the cathode with great velocity, and which are charged with negative electricity. We might similarly conceive that radium sends into space negatively electrified particles.

A specimen of radium, enclosed in a solid thin perfectly insulated envelope, should become spontaneously charged to a very high potential. By the ballistic hypothesis the potential would increase until the potential difference of the surrounding conductors became sufficient to hinder the ejection of the electrified particles and to cause their return to the source of radiation.

We have performed an experiment on these lines. A specimen of very active radium was enclosed for some time in a glass vessel. In order to open the vessel, we made a trace on the glass with a glass cutter. Whilst so doing, we clearly heard the report of a spark, and upon examining the vessel with a magnifying glass, we observed that the glass had been pierced by a spark at the spot where it had been weakened by the scratch. The phenomenon produced is comparable to the rupture of the glass of an overcharged Leyden jar.

The same phenomenon occurred with another glass. Further, at the moment of the passing of the spark, M. Curie, who was holding the glass, felt the electric shock of discharge in his fingers.

Certain kinds of glass have good insulating properties. If the radium is enclosed in a sealed glass vessel, well insulated, it is to be expected that, at a given moment, the vessel will be spontaneously perforated.

Radium is the first example of a body which is spontaneously charged with electricity.

Action of the Electric Field upon the Deflected β-Rays of Radium.

The β-rays of radium, being analogous to the cathode rays, should be deflected by an electric field in a manner similar to the latter; *i.e.*, as would a particle of matter negatively charged and hurled into space with a great velocity. The existence of such a deflection has been demonstrated both by M. Dorn and M. Becquerel.

Let us consider the case of a ray which traverses the space situated between the two plates of a condenser. Suppose the direction of the ray parallel to the plates: when an electric field is established between the latter, the ray is subjected to the action of this uniform field along its whole path in the condenser *l*. By reason of this action the ray is deflected towards the positive plate and describes the arc of a parabola; on leaving the field, it continues its path in a straight line, following the tangent to the arc of the parabola at the point of exit. The ray can be received on a photographic plate perpendicular to its original direction. Observations are taken of the impression produced on the plate when the field is zero, and when it has a known value, and from that is deduced the value of the deflection, δ, which is the distance of the points in which the new direction of the ray and its original direction meet a common plane perpendicular to the original direction. If *h* is the distance of this plane from the condenser, *i.e.*, at the edge of the field, we have, by a simple calculation,—

$$\delta = \frac{e\,\mathrm{F}\,l\left(\frac{l}{2}+h\right)}{mv^2};$$

m being the mass of the moving particles, *e* its charge, *v* its velocity, and F the strength of the field.

The experiments of M. Becquerel enable him to assign a value approaching to δ.

Relation of the Charge to the Mass for a Particle Negatively Charged emitted by Radium.

When a material particle having a mass *m* and a negative charge *e*, is projected with a velocity *v* into a uniform magnetic field perpendicular to its initial velocity, this particle describes, in a plane normal to the field and passing through its initial velocity, an arc of a circle of radius ρ, so that—H being the strength of the field—we have the relation—

$$\mathrm{H}\,\rho = \frac{m}{e}v.$$

If, for the same ray, the deflection, δ, and the radius of curvature, ρ, be measured in a magnetic field, values could be found from these two experiments for the ratio $\frac{e}{m}$ and for the velocity, *v*.

The experiments of M. Becquerel threw the first light upon this subject. They gave for the ratio $\frac{e}{m}$ a value approximately equal to 10^7 absolute electro-magnetic units, and for *v* a magnitude $1{\cdot}6 \times 10^{10}$. These values are of the same order of magnitude as those of the cathode rays.

Accurate experiments have been made upon the same subject by M. Kaufmann. This physicist subjected a narrow beam of radium rays to the simultaneous action of an electric field and a magnetic field, the two fields being uniform and having a similar direction, normal to the original direction of the beam. The impression produced on a plate normal to the primitive beam and placed beyond the limits of the field with reference to the source, has the form of a curve, each point of which corresponds to one of the rays of the original beam. The most penetrating and least deflected rays are at the same time those with the greatest velocity.

It follows from the experiments of M. Kaufmann that, for the radium rays, of which the velocity is considerably greater than that of the cathode rays, the ratio $\frac{e}{m}$ decreases, while the velocity increases.

According to the researches of J. J. Thomson and Townsend, we may assume that the moving particle, which constitutes the ray, possesses a charge, *e*, equal to that carried by an atom of hydrogen during electrolysis, this charge being the same for all the rays. We are therefore led to the conclusion that the mass of the particle, *m*, increases with increase of velocity.

These theoretical considerations lead to the idea that the inertia of the particle is due to its state of charge during motion, the velocity of an electric charge in motion being incapable of modification without expenditure of energy. To state it otherwise, the inertia of the particle is of electro-magnetic origin, and the mass of the particle is—in part at least—a virtual mass or an

electro-magnetic mass. M. Abraham goes further, and assumes that the mass of the particle is entirely an electro-magnetic mass. If, according to this hypothesis, the value of this mass, m, be calculated for a known velocity, v, we find that m approaches infinity when v approaches the velocity of light, and that m approaches a constant value when the velocity, v, is much less than that of light. The experiments of M. Kaufmann are in agreement with the results of this theory, the importance of which is great because it foreshadows the possibility of establishing mechanical bases upon the dynamical of little particles of matter charged in a state of motion.

These are the figures obtained by M. Kaufmann for $\frac{e}{m}$ and v.

$\frac{e}{m}$. Electro-magnetic units.	v $\frac{\text{c.m.}}{\text{sec.}}$	
$1{\cdot}865 \times 10^7$	$0{\cdot}7 \times 10^{10}$	For cathode rays (Simon).
1·31 ,,	2·36 ,,	For radium rays (Kaufmann).
1·17 ,,	2·48 ,,	
0·97 ,,	2·59 ,,	
0·77 ,,	2·72 ,,	
0·63 ,,	2·83 ,,	

M. Kaufmann concludes, from comparison of his experiments with the theory, that the limiting value of the ratio $\frac{e}{m}$ for radium rays of relatively small velocity would be the same as the value $\frac{e}{m}$ for cathode rays.

The most complete experiments of M. Kaufmann were made with a minute quantity of pure radium chloride, with which we provided him.

According to M. Kaufmann's experiments, certain β-rays of radium possess a velocity very near to that of light. These rapid rays seem to possess great penetrating capacity towards matter.

Action of the Magnetic Field upon the α-Rays.

In a recent work, Mr. Rutherford announced that, in a powerful electric or magnetic field, the α-rays of radium are slightly deflected, in the manner of particles positively electrified and possessing great velocity. Mr. Rutherford concludes from his experiments that the velocity of the α-rays is of the order of magnitude $2{\cdot}5 \times 10^9$ $\frac{\text{c.m.}}{\text{sec.}}$ and that the ratio $\frac{e}{m}$ for these rays is of the order of magnitude 6×10^3, which is 10^4 times as great as for the deflected β-rays. We shall see later that these conclusions of Mr. Rutherford are in agreement with the properties already known of the α-radiation, and that they account, in part at least, for the law of absorption of this radiation.

The experiments of Mr. Rutherford have been confirmed by M. Becquerel. M. Becquerel has further demonstrated that polonium rays behave in a magnetic field like the α-rays of radium, and that, for the same field, they seem to have the same curvature as the latter.

It also appears from M. Becquerel's experiments that the α-rays do not form a magnetic spectrum, but act rather like a homogeneous radiation, all the rays being equally deflected.

Action of the Magnetic Field on the Rays of other Radio-active Substances.

We have just seen that radium gives off α-rays comparable to the tube rays, β-rays comparable to cathode rays, and γ-rays which are penetrating and not deflected. Polonium gives off α-rays only. Amongst the other radio-active substances, actinium seems to behave like radium, but the study of its radiation has not yet advanced so far as in the case of radium. As regards the faintly radio-active bodies, we know to-day that uranium and thorium give rise to α-rays as well as β-rays (Becquerel, Rutherford).

(To be continued).

A NEW METHOD FOR THE DETECTION AND ESTIMATION OF THE MINUTEST TRACES OF ARSENIC.

By ARMAND GAUTIER.

During the course of my publications on the detection and estimation of small quantities of arsenic (*Comptes Rendus*, vol. lxxxi., p. 239; *Ann. Chim. Phys.*, Series 5, vol. viii., p. 384), especially when I wished to demonstrate the normal existence and the localisation of this metalloid in the organs of animals (*Comptes Rendus*, vol. cxxix., pp. 929 and 936; vol. cxxx., p. 284; vol. cxxxiv., p. 1394; *Bull. Soc. Chim.*, Series 3, vol. xxvii., pp. 135 and 833), I found it necessary to verify, first of all, the important point of knowing if the method of nitrosulphuric carbonisation that I had used since the year 1875, would enable me to collect the whole of the arsenic without any loss. More recently, I have shown that this method is sufficiently precise to enable two-thousandths, or even one-thousandth of a m.grm. of arsenic to be recovered from 100 grms. of animal or vegetable matter, without loss; that is, in 50 or 100 million times its weight of foreign organic matter (*Bull. Soc. Chim.*, Series 3, vol. xxix., p. 639).

Thus it would not appear as if there was room to attempt to improve so exact a method. However, it is so delicate in its application, it requires the use of so many reagents (distilled water, sulphuric and nitric acids, sulphuretted hydrogen, ammonia, sulphurous acid, bisulphites, zinc, &c.), that there may be some room for doubt, when we are dealing with infinitesimal quantities of arsenic, the thousandth of a m.grm., and less, in comparatively large quantities of animal or vegetable matter. I shall show that distilled water, ammonia supposed to be pure, pure nitric acid, sulphurous acid, and, above all, sulphuretted hydrogen well washed with acids and water, always contain traces of arsenic. In the experiments I have just concluded, after the purification of all these reagents, the total amount of arsenic used in an experiment for its detection in 100 grms. of muscle or yolk of egg, was from one-half to three-quarters of a thousandth of a m.grm. of the metalloid.

Another reason has caused me to attempt to simplify my old method. It cannot be applied when it is a question of recovering the arsenic in substances very rich in soluble chlorides, such as sea-water, highly chlorised mineral waters, salt meats, kitchen salt, or in solutions too rich in iron, as will be seen later on. No matter what we do, the arsenic is partially lost in the above cases, either in the form of chloride, which escapes without being decomposed, even passing alkaline water, or in the state of sulpharseniate of iron.

The new method I am about to describe is of extreme simplicity and of remarkable accuracy. It can be used for the physiological determination of traces of arsenic as well as for expert legal work, but I will confine myself, for the time being, to a description of the method and the results obtained in cases where the old methods are inapplicable or uncertain.

This method is founded, in principle, on the well-known observation, that when arsenic exists, even in very small quantities, in the presence of iron in a potable or mineral water, the latter by oxidation and precipitation always carries with it a part or the whole of this arsenic.

My recent researches have shown that this property of iron is *absolute*, and that this entanglement of the arsenic by the ferric sub-salts is so complete, under the experimental conditions I adopted, that 1/100oth of a m.grm. of arsenic added in the form of arsenite or arsenate to a litre of pure water, or water containing sea-salt or other salts, was entirely removed by the iron, and could be estimated easily and directly by placing the precipitate re-dissolved in dilute sulphuric acid in the Marsh apparatus.

I prepare my reagent in the following manner:—100 grms. of commercial ferrous sulphate are dissolved in 500

grms. of distilled water, with the addition of 25 grms. of pure sulphuric acid, and treated with sulphuretted hydrogen. Boil and filter; then, while still warm, oxidise the ferrous salt by means of 28 grms. of nitric acid free from arsenic. The ferric hydrate is then precipitated by ammonia free from arsenic, and, after washing, the ferric hydrate is re-dissolved in cold, pure, dilute sulphuric acid. This ferric sulphate still contains appreciable traces of arsenic (0·002 to 0·003 m.grm. of arsenic in 3 grms. of Fe_2O_3). This is removed by digesting the ferric solution for two days with pure granulated zinc and then boiling *in vacuo* (P. Clausmann). The salt is then re-oxidised with a little nitric and sulphuric acids, and the ferric hydrate precipitated by a slight excess of pure ammonia, which re-dissolves the zinc. There now remains only to wash and to add pure, dilute, cold sulphuric acid to the ferric hydrate thus prepared. One hundred c.c. of this reagent containing 30 grms. of Fe_2O_3 per litre gave, by the method I am about to describe, a ring corresponding to less than half a thousandth of a m.grm. of arsenic. Five c.c. of this solution are sufficient to precipitate the arsenic in 300 or 400 c.c. of water, so it is obvious that only 0·0000025 m.grm. (practically none at all) of arsenic is introduced through this reagent. With this reagent the following observations can be made :—

If we take two litres of distilled water and evaporate them in the presence of 40 grms. of nitric acid and 10 grms. of sulphuric acid practically free from arsenic (they contain together less than 0·0001 m.grm. of arsenic), and after driving off the nitric acid, we dilute with water and pour the whole into the Marsh apparatus, we obtain :—

	Arsenic per litre. M.grm.
Water distilled in a tinned copper retort ..	0·0007
Water distilled in a glass retort, after adding 5 grms. per 1000 of pure CO_3Na_2	0·0010

A litre of this slightly arsenical water is boiled after the addition of 5 c.c. of the above ferric solution; after cooling, it is saturated with pure ammonia, boiled again for a few moments, and then filtered. The solution evaporated in the presence of pure nitric and sulphuric acids is concentrated, heated to drive off the nitric acid, diluted with water, and placed in the Marsh apparatus. *It does not give any trace of arsenic.* (At least no appreciable trace; that is to say, a smaller quantity than 0·00033 m.grm. of arsenic).

To 2 litres of this water thus freed from arsenic, we add 0·002 m.grm. of arsenic in the form of arsenite of soda, then 5 c.c. of the ferric solution. Boil, make slightly alkaline, and collect the precipitate which is dissolved in a slight excess of sulphuric acid; the sulphate formed is poured directly into the Marsh apparatus. In this manner we found :—*Arsenic added* to 2 litres of water, 0·002 m.grm.; *arsenic found*, 0·002 m.grm. Thus the total amount of arsenic present was carried down.

The same is the case if water treated in this manner with one-thousand millionth of its weight of arsenic is evaporated down to one-quarter its volume, and then treated with the ferric salt as above.

Thus one-thousandth of a m.grm. per litre of water is collected entirely by the ferric precipitate formed, and can be estimated exactly, rapidly, and correctly by Marsh's apparatus.

As a check, to 1 litre of distilled water we added 0·050 m.grm. of arsenic, then 5 c.c. of the ferric solution; boil, and filter after neutralisation with pure ammonia. The filtered liquor is treated as above with 20 grms. of nitric acid and 10 grms. of sulphuric acid; the excess of water and nitric acid is driven off by heat, and the remainder transferred to the Marsh apparatus. The amount of arsenic found is *nil*.

Thus, by this method we are enabled to detect and estimate exactly and without loss, a substance which is present to the extent of one part in one-thousand million parts of the material under examination.

I do not think that up to the present in experimental science or in any observations whatsoever, any other determination has been made with so great a degree of accuracy.

The same method may be applied with equal accuracy to waters highly charged with sea-salt (300 grms. per litre, pure or impure) of sulphate of potassium, nitre, chlorate of potassium, &c.

Consequently, we are enabled to estimate with precision the arsenic present in sea-water, in sea-salt, in mineral waters, the ordinary salts, acids, and bases, &c., with rapidity and perfect exactitude. It is only necessary to operate in neutral solution.

As for the application of this new method to the physiological or medico-legal detection of arsenic in the organs, we can first destroy the animal or vegetable matter by means of the nitrosulphuric mixture, and then take up the residue with boiling water; filter, cool, *partially* neutralise, and add the ferric solution so long as it does not show with ferrocyanide. The precipitate formed in the cold does not carry down the arsenic under these conditions. Filter again, add 5 c.c. of the ferric reagent, and bring the solution to boiling. After neutralisation with ammonia, filter, re-dissolve the ferric precipitate in a mixture of pure nitric and sulphuric acids, heat until all the nitrous fumes are given off and only nitric acid remains; dilute with water, and then pour direct into the Marsh apparatus. For complete success in the above case, this method requires a series of minute precautions which I shall make known in another paper.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 16.

INTENSIFICATION OF CHEMICAL ACTION BY THE EMANATIONS FROM GOLD AND PLATINUM.*

By G. T. BEILBY.

When a piece of gold or platinum foil is heated on a glass slip in an atmosphere containing the products of combustion of coal-gas a halo is formed on the glass surface surrounding the foil. This halo does not to any considerable extent consist of metallic particles, but is chiefly made up of the products of decomposition of the glass. If the halo is breathed on, the slight condensation of moisture on the surface dissolves the soluble salts, and sets free silica or an insoluble silicate in the form of thin films and spicules. When the water has evaporated a crystalline deposit is left on the surface.

By prolonged heating in the above atmosphere the whole of the exposed surface of the glass slip is slightly attacked, but the intensity of this attack is not to be compared with that which occurs in the near neighbourhood of the metal. The chemical action to which the formation of the halo is due, is therefore directly influenced by the presence of the hot metal.

It was at first thought that the metal foil might be acting simply by arresting radiant heat in its passage through the transparent glass, and thereby localising its effects; but this view is not supported by the subsequent experiments.

A number of experiments were made before it was sufficiently realised that a fairly free circulation of the atmosphere surrounding the metal is necessary if well marked halos are to be produced. It was also found that the partial exclusion of the products of combustion from the air-bath adversely affected the formation of halos.

When the glass slip with the metal foil is covered by another slip which is in contact with the metal, the halo is reduced to a sharp narrow outline of the foil.

If the cover slip is supported just out of contact with the metal, the halo is still a sharp outline, but now an image of the foil, less sharp, but also in outline, is formed on the

* Abstract of a Paper read before the British Association (Section A), Southport Meeting, 1903.

under surface of the cover slip. As the distance between the cover slip and the foil is increased, the halo widens and the image on the cover slip becomes a smooth patch without sharp outlines. These effects are obviously influenced by the more or less ample supply of the active constituents of the atmosphere which results from the greater or less freedom of circulation. This, in turn, is affected by the nearness of the cover slip to the metal.

A piece of platinum foil, 7 m.m. square, was used in a series of experiments in which the distances of the upper slip from the metal were 0·2 m.m., 1·5 m.m., 3 m.m., and 7 m.m.; an experiment was also made in which no cover slip was used. The temperature employed was about 500°, and the time of heating thirty minutes. At 0·2 m.m. distance halo and image* were both in outline. At 1·5 m.m. the halo was a band round the foil about 1 m.m. wide; the image showed no outline, but was in size and form similar to the foil. At 3 m.m. the halo had widened to over 2 m.m., part of this being got by encroaching on the area covered by the foil; the image was now circular, its diameter being equal to the diagonal of the square of the foil. At 7 m.m. the halo had widened to 3 to 4 m.m. on three sides, and to 8 m.m. on the fourth side; its general form was oval. The image was of the same form, and only a little smaller. It was evident in this case that the stream of emanations from the platinum had drifted across the slip under the influence of a current in the atmosphere of the air-bath. This evidence of drifting of the stream of emanations at once disposes of the idea that the formation of the halo and image is due in any way to the radiation or reflection of heat by the metal foil. The forms and dimensions of the halos and images strongly suggest that the emanations from the platinum are thrown upwards like a fountain, which spreads and descends on and around the foil. When the cover slip is at the maximum distance it is struck by the apex of the stream, and a large but faintly defined image is produced. When the distance of the cover slip is small, the stream is intercepted before it has spread much, and the halo and image are small and well-defined.

The decomposition of glass in the neighbourhood of hot metals appears to be a case of accelerated or intensified chemical action induced by the energy of the particles shot out from the hot metal. It occurred to me that some of the cases of catalytic action by platinum and other substances might be accounted for by the existence of active emanations surrounding the catalyte, and not merely by the actual contact of the molecules of the reagents with its surface. Experiments are now in progress to test this question.

ACTION OF MALT DIASTASE ON POTATO-STARCH PASTE.†

By ARTHUR R. LING.

Brown and Millar have shown that the so-called stable dextrin—one of the products of the hydrolysis of potato-starch paste by diastase—is converted by the further action of diastase into a mixture of about equal parts of *d*-glucose and maltose. The observation of Davis and Ling (see next abstract) that no *d*-glucose is formed when unrestricted diastase acts on starch paste, stands in apparent antithesis to this. However, the author has confirmed the result of Brown and Millar, and has found further that other isolated products of diastatic action yield a proportion of *d*-glucose when submitted to the further action of unrestricted diastase; thus the maltodextrin, *a* of Ling and Baker, when treated in 3 per cent solution with an active preparation of diastase at 55° for 140 hours, gave the constants $[\alpha]_{D\ 3\cdot93}$ 127·6°, $R_{3\cdot93}$ 105·6, corresponding approximately with maltose 90 per cent, *d*-glucose 10 per cent. The presence of 10·5 per cent of *d*-glucose in the product was proved by weighing the phenylglucosazone formed under standard conditions. Taking into account the fact that potato-starch paste is never completely converted into maltose, although the final product has the constants of that sugar, and that a substance is always present which is identical with the isomaltose of C. J. Lintner, the simple dextrin of Ling and Baker, and the dextrinose of Syniewski, which, when isolated and submitted to the action of diastase, yields *d*-glucose, the author suggests that the reason no *d*-glucose can be detected among the products of the action of unrestricted diastase on starch paste is that that sugar is immediately condensed by the action of the enzyme forming dextrinose. When, however, diastase is pre-heated, its condensing action is weakened, and the *d*-glucose formed can be isolated. Attempts to condense *d*-glucose or mixtures of it with maltose have not been successful.

* Throughout this paper the term "halo" is applied to the effect produced on the lower slip on which the metal lay, and "image" to that on the under surface of the cover slip.

† A Paper read before the British Association (Section B), Southport Meeting, 1903.

ACTION OF MALT DIASTASE ON POTATO-STARCH PASTE.*

By BERNARD F. DAVIS, B.Sc., and ARTHUR R. LING.

In a previous paper (*Journ. Fed. Inst. Brew.*, 1902, viii., 475) it was shown that when malt diastase is heated in aqueous solution above the temperature at which the activity of the enzyme is at its optimum, namely 55°, the reaction with potato-starch paste at about 55° is not only slower, but different products are formed; thus *d*-glucose can be readily isolated from them after the reaction has been allowed to proceed for several hours. Special experiments, employing the same quantities of diastase which has not been heated in solution above 55°, show that *d*-glucose is not formed either from starch paste or from maltose. It therefore appears that the production of this sugar is connected with the pre-heating of the hydrolytic agent in solution above 55°. As a result of a very large number of new experiments, which will be published soon, the authors have arrived at the following conclusions:—

The effect of heating a solution of diastase as above indicated is to weaken its action and also to produce an alteration in the enzyme molecule, which is moreover a permanent one, for the diastase retains its altered properties when re-precipitated from its solution by alcohol and allowed to act on starch paste at or below 55°. The alteration of the diastase is assumed by the production of *d*-glucose when it acts on starch paste, and it appears to commence when a solution of the enzyme is heated below 60°; although, judging from the small amount of *d*-glucose formed by its action, the change at the last-named temperature is not complete. As the temperature of pre-heating the solution is increased, the amount of *d*-glucose it is capable of producing also increases, the maximum amount being obtained by the action of diastase which has been pre-heated in solution at 68° to 70° for fifteen to thirty minutes. Above this temperature the destruction of the enzyme is so rapid that a much larger proportion of it has to be employed to attain the stage of the reaction at which *d*-glucose appears. Still *d*-glucose is formed by diastase which has been restricted at temperatures up to 78°, and probably above this. It has been observed in all cases that, when after the maximum amount of *d*-glucose has been formed, the solution is kept at the temperature of hydrolysis, usually 55°, the sugar just mentioned diminishes in amount, and the occurrence of this apparent condensing action of the enzyme may probably explain the failure in several cases to detect *d*-glucose among the products of

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

hydrolysis (compare the preceding paper). The maximum amount of *d*-glucose formed in any case does not exceed about 12 per cent of the total hydrolytic products.

THE CHEMICAL AND PHYSICAL CHARACTERS OF THE SO-CALLED "MAD-STONE."*

By Dr. H. C. WHITE.

It is a widespread current superstition in the Southern States of America that the sting of a *venomous* snake and the bite of a *rabid* animal (dog, &c.) may be *detected* and discriminated from an innoxious wound, and the venom of the wound *extracted* by application of what is called the "mad-stone." Several of these stones came opportunely into the hands of the author, and an examination of their character was made.

The "mad-stone" of current superstition is a very rare concretionary calculus found in the gullet of the male deer. As extracted it resembles a water-worn pebble, oblong in form, varying in size, but not greater, perhaps, than 3 inches in length by 1½ inch in thickness. A smooth flat surface is given to one side by rasping. The examination was directed to the following points:—

1. *Chemical Composition.*—Found to be chiefly tri-calcic phosphate. Exact figures of analyses given.

2. *Adherence to Cut and Torn Flesh-wounds.*—Found to vary with the mechanical character of the wound and the mode of application of the stone, without regard to venomous or non-venomous character of the wound.

3. *Absorbing Power.*—Immersed in water the stones were found to absorb to an extent of 5 per cent of their weight. Applied to fresh wounds and carefully adjusted, blood and other fluid absorbed to a maximum extent of 2·3 per cent the weight of the stone.

4. *Character of Matter Absorbed.*—The stone after application to the wound is boiled with water, or *milk* (in accordance with the superstition). The fluid is discoloured, and is shown to be *toxic* in the case of a known venomous wound. No difference in discolouration observable in venomous and non venomous wounds. That the stones are not *curative* is shown by the death of animals from venomous wounds after application of the stone.

The literature of the subject has been examined. The "mad-stone" superstition seems quite ancient. It was current in New England in Puritan times. The author has in his possession an authenticated "mad-stone" dating from 1654. This, however, is a moderately porous *sandstone*, entirely different from the modern "mad-stone" of the Southern States. It is peculiar in form, and appears somewhat as a water-worn pebble.

Specimens of the current "mad-stone" were exhibited in illustration of the paper.

Formation of Lactic Acid by the Action of Caustic Potash on the Pentoses.—K. Katsuyama.—Araki has shown that arabinose heated with soda-lye gives rise to the formation of formic and lactic acids. As xylose has quite a different constitution formula to arabinose, and as the recent researches of Salkowski show that the putrid fermentation of this sugar gives C_2H_5OH in considerable proportions, and as that of xylose does not give a trace of this alcohol, it appeared of interest to examine the action of KOH on xylose. The research described in this paper establishes the fact that this sugar is transformed, under these conditions, into lactic acid of fermentation. The same experiments made with arabinose confirm the results published by Araki; that is to say, they lead also to the formation of lactic acid of fermentation starting with arabinose.—*Berichte*, vol. xxxv., p. 669.

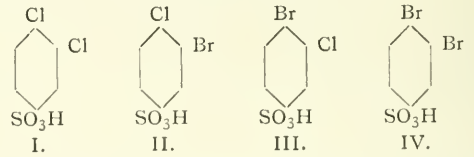
* A Paper read before the British Association (Section B), Southport Meeting, 1903.

ISOMORPHOUS SULPHONIC DERIVATIVES OF BENZENE.*

The object the Committee have primarily in view is the crystallographic study of the complete series of sulphochlorides and sulphobromides derived from the isomeric dichloro-, dibromo-, and chlorobromo-benzenes.

The results obtained in the case of the para- and two of the three series of meta-derivatives have been referred to in previous reports. It may be pointed out that whereas no evidence was obtained that the 1 : 4-derivatives exist in polymorphic forms, the five compounds measured being strictly isomorphous,† in the case of the meta-derivatives, the 1 : 3 : 4-series formed an isotrimorphous group, the 1 : 3 : 5-series an isotetramorphous group.

During the past year Mr. Harding has determined the constants of five of the eight members of the 1 : 2 : 4-ortho-series, viz., the chlorides derived from the acids Nos. I., II., and IV., and the bromide of acid No. II. :—



Of the chlorides, I. and II. are practically identical crystallographically; the chloride of IV. was obtained in quite a distinct form, belonging, however, to the same crystallographic system. The bromide of II. was obtained in both these forms, so that it establishes a connecting-link between the two isomorphous series which evidently exist.

Great difficulty was experienced in making the measurements, owing to the low melting-points of the sulphonhalides and the extraordinary way in which they crystallise (from a mixture of benzene and petroleum) in very thin micaceous plates; it was discovered, however, that by using petroleum of higher boiling-point more massive crystals could be obtained; forms fit for measurement were eventually secured by this artifice.

It would seem that the character of the solvent has a definite influence on crystalline form, especially in the case of substances which manifest polymorphism. When opportunity offers it will undoubtedly be desirable to study this question experimentally.

The anilides, which have higher melting-points than the halides, crystallise with much greater facility; the opportunity has been taken to study several of these. Mr. Harding finds that the orthodichloranilide exists in two forms—one orthorhombic, the other monosymmetric; and that whilst the dibromo- and bromochlor-anilides crystallise in a form isomorphous with the monosymmetric form of the dichloranilide, the fourth anilide crystallises in a second monosymmetric form.

Mr. Harding has also measured the 1 : 3-dibromo-2-sulphochloride, and has thus made a beginning with the 1 : 2 : 3-meta-series.

Although the material is available, it has been impossible hitherto to obtain two of the para-compounds and three 1 : 2 : 4-derivatives in forms suitable for measurement; it is hoped that the difficulty will be overcome, and that the experience which has been gained will make it possible to extend the investigation to the remaining terms of the meta- and ortho-series at no distant date. It is very desirable, for this purpose, to have large quantities of material at disposal, and that special apparatus should be devised which will make it possible to effect the crystallisation under constant conditions.

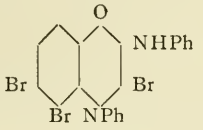
* Fourth Report of the Committee, consisting of Prof. H. A. Miers (Chairman), Dr. H. E. Armstrong (Secretary), Prof. W. P. Wynne, and Prof. W. J. Pope. (Drawn up by the Secretary). Read before the British Association (Section B), Southport Meeting, 1903.

† Mr. Harding has recently been able to obtain a sixth member of this series—the 1Cl : 4Br : 3-sulphobromide—in measurable form, and finds that it is isomorphous with five which Mr. Gidden measured. Mr. Gidden did not succeed in preparing this compound.

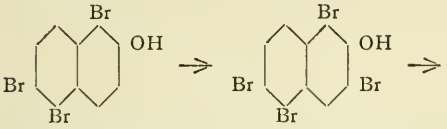
ISOMERIC NAPHTHALENE DERIVATIVES.*

During the past year proof has been obtained of the structure of the series of higher brominated derivatives prepared from 1 : 5 : 6-tribromo-β-naphthol which were referred to in last year's report; these compounds were then represented by formulæ containing a bromine atom in position 3 marked with a query. The following facts show that a correct view was then taken as to the position of this bromine atom.

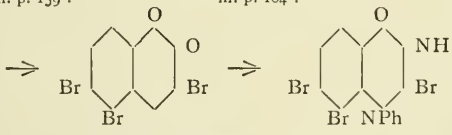
The tetrabromo-β-naphthol (m. p. 184°), from which the higher brominated compounds are derived, is convertible by nitric acid into a tribromo-β-naphthaquinone (m. p. 183°), which aniline converts into the compound—



Such a substance can obviously only be formed from a quinone containing a bromine atom in position 3, not from one containing bromine in the alternative position 4. The relationship of the several compounds is therefore as follows :—



Tribromo-β-naphthol, m. p. 159°. Tetrabromo-β-naphthol, m. p. 184°.

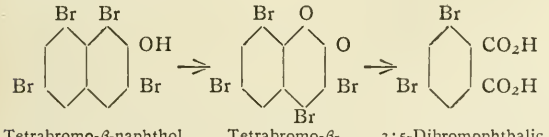


Tribromo-β-naphthaquinone, m. p. 183°. Anil.

The structure has also been determined of the tetrabromo-β-naphthol, No. 3 (m. p. 191°; *acetate*, m. p. 210°), described in the 1901 report, which differs from all the other highly brominated naphthols in that it fails to give a nitro-bromo-keto-compound, being converted by nitric acid at the ordinary temperature into a tetrabromo-β-naphthaquinone (m. p. 241°).

This tetrabromo-β-naphthaquinone is oxidised by dilute nitric acid to a new dibromophthalic acid, which, by exclusion, must be the hitherto unknown 3 : 5-*dibromophthalic acid;* the quinone is therefore 3 : 4 : 6 : 8-*tetrabromo-β-naphthaquinone*.

The parent naphthol, which is derived from 1 : 3 : 6-tribromo-, not from 1 : 5 : 6-tribromo-β-naphthol, must therefore contain the bromine atoms in positions 1 : 3 : 6 : 8, the series of compounds being related as shown by the following formulæ :—



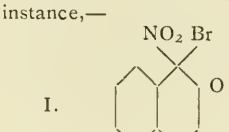
Tetrabromo-β-naphthol, m. p. 191°. Tetrabromo-β-naphthaquinone, m. p. 241°. 3:5-Dibromophthalic acid, m. p. 188°; *anhydride*, m. p. 155°.

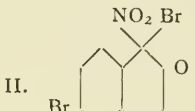
It follows from these results that, whilst the product of the further bromination of 1 : 3 : 6-tribromo-β-naphthol is 1 : 3 : 4 : 6-tetrabromo-β-naphthol, small quantities of the 1 : 3 : 6 : 8-tetrabromo-derivative are also formed.

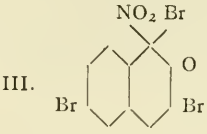
* Report of the Committee, consisting of Prof. W. A. Tilden (Chairman, and Dr. H. E. Armstrong (Secretary). (Drawn up by the Secretary). Read before the British Association (Section B), Southport Meeting, 1903.

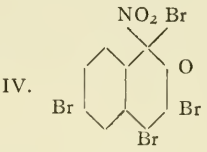
The investigation of the bromo-naphthols has involved incidentally the study of the bromophthalic acids; the discovery of 3 : 4- and 3 : 5-dibromophthalic acids in the course of the work completes the series of dibromo-acids.

A systematic investigation of the nitro-bromo-keto-compounds formed by the action of nitric acid on the bromo-β-naphthols has led to the important discovery that whereas most of these substances are of normal composition—for instance,—

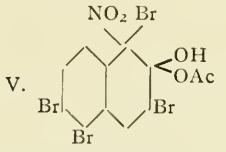


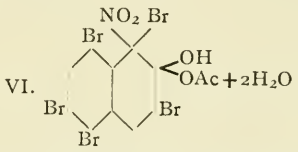






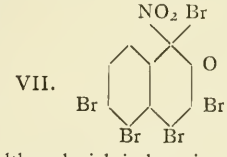
others can only be obtained in association either with acetic acid alone or with water of hydration. Thus—

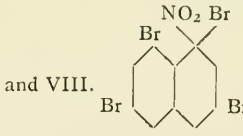




A similar addition of acetic acid takes place in the case of the keto-bromides (*infra*), but apparently not in the case of the keto-chlorides. These, however, as Zincke's researches show, in a few cases combine with alcohol.

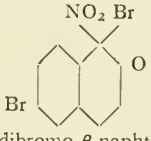
Generally speaking, the nitro-bromo-keto-compounds increase in stability as the number of bromine atoms increases, so that, whilst the compound I., for instance, begins to decompose slightly above 0°, the compound II. is so stable that it may be left exposed during several months in the air at the ordinary temperature without undergoing change. But that structure and not merely the proportion of bromine present in the compound largely determines stability is shown by the fact that, for example, the compounds represented by the formulæ—



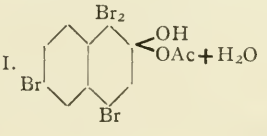


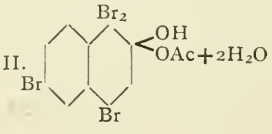
although rich in bromine, rapidly decompose at the ordinary temperature.

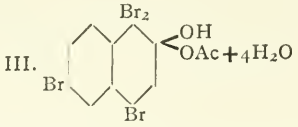
When bromine (one molecular proportion) is left in contact with the nitro-keto-compound—



(derived from 1 : 6-dibromo-β-naphthol), suspended in glacial acetic acid and exposed to diffused light, nitrous fumes are slowly evolved and an arborescent mass of needles separates which appears to be the mono-hydrate (I.) of the acetate of a dibromo-naphthalene-keto-bromide—

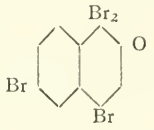




III. 

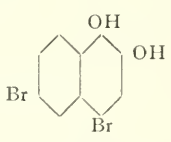
This substance melts at 63—65°; from the mother-liquors large slightly yellow prisms slowly separate which consist of the tetrahydrate III. The dihydrate II. is formed only under very special conditions, namely, when a solution of the nitro-bromo-keto-compound from 1-bromo-β-naphthol in acetic acid is acted on by bromine; it separates very slowly from solution in the form of small nearly colourless needles, melting at 81°.

If any one of these hydrated acetates be gently warmed with benzene a turbid solution is obtained; if this be dried with the aid of calcium chloride and slowly evaporated, it deposits magnificent nearly colourless plates of the simple keto-bromide,—



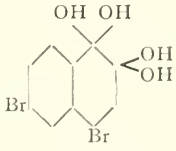
This substance apparently is the first representative of the class of naphthalene keto-bromides corresponding to the keto-chlorides which have been so fully studied by Zincke. When gently warmed, either alone or in the form of one of its hydrated acetates, with glacial acetic acid, it loses bromine and is converted into 4 : 6-dibromo-β-naphthaquinone (m. p. 171°); if the warming be continued the liberated bromine acts on this compound, converting it into 3 : 4 : 6-tribromo-β-naphthaquinone (m. p. 190°). Care is necessary, however, as otherwise the action may go further; a pentabromo-dinaphthyl-diquinone, $C_{20}H_5Br_5O_4$, then separates as a yellow crystalline insoluble powder. This compound is formed according to the equation $2C_{10}H_3Br_3O_2 = HBr + C_{20}H_5Br_5O_4$. A similar case of condensation was mentioned in last year's report.

Unlike the keto-chlorides, the keto-bromides do not give substituted naphthols when reduced either with stannous chloride and chlorhydric acid or with iodhydric acid (density 1·9); the sole product is 4 : 6-dibromo-1 : 2-dihydroxy-naphthalene,—

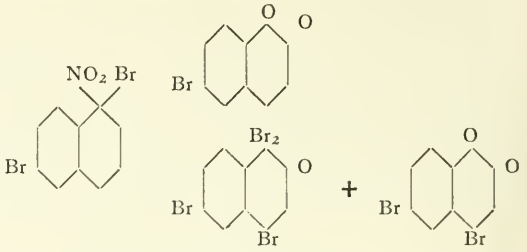


which is also obtained by reducing 4 : 6-dibromo-1 : 2-naphthaquinone. The corresponding diacetate, $C_{10}H_4Br_2(OAc)_2$, crystallises in large prisms melting at 157°.

The keto-bromide is probably first transformed into—



The discovery of 4 : 6-dibromo-2-keto-naphthalene-1-dibromide makes it possible to explain the production of 4 : 6-dibromo-1 : 2-naphthaquinone during the decomposition by heat of the nitro-keto-compound of 1 : 6-dibromo-β-naphthol. That the dibromo-quinone could not be formed by a mere bromination of 6-monobromo-β-naphthaquinone initially produced is shown by the fact that this bromination cannot be realised in practice. The real explanation is that the bromine initially split off from the nitro-keto-compound brominates the undecomposed remainder of this substance, first displacing NO_2; a subsequent decomposition produces the 4 : 6-dibromo-quinone.



Now that the investigation has reached a stage when it is possible to give a complete account of the complex series of processes underlying the formation of the brominated naphthols, it is proposed to submit a considered discussion of the results for publication.

ON THE REDUCTION OF NITRATES BY SEWAGE.*

By Prof. LETTS, D.Sc., Ph.D., R. F. BLAKE, F.C.S., F.I.C., and J. S. TOTTON, B.A.

THE object of this investigation was to ascertain to what extent, and with what rapidity, the nitrogenous constituents of sewage can be broken down by a suitably arranged scheme of purification, so that their nitrogen is evolved in the gaseous state. It is well known that in the most efficient systems of sewage purification by natural methods the resulting effluent is comparatively free from ammonia and organic nitrogen, but is charged with nitrates. These latter, however, do not correspond in amount with the quantities of the two former originally present, but are always less, and one of the authors, in conjunction with another chemist, has shown that during the treatment of sewage by the so-called "contact" or "bacteria" beds a considerable quantity of the combined nitrogen escapes as free nitrogen ("On the Chemical and Biological Changes Occurring during the Treatment of Sewage by the so-called Bacteria Beds," by Prof. Letts, D.Sc., Ph.D., and R. F. Blake, F.C.S., *B. A. Rep.*, 1901).

The researches of Gayon and Dupetit, Tacke, Adeney, and others have shown that nitrates are themselves decomposed when in contact with sewage with evolution of nitrogen or its oxides, and carbonic anhydride.

It therefore seemed possible that by a judicious combination of the two processes, *i.e.*, production and destruction of nitrates, a considerable proportion and possibly most of the combined nitrogen present in sewage might be converted into free nitrogen, and as a consequence the resulting effluent be deprived of its fertilising properties in relation to vegetation.

Such a result might appear useless, and even wasteful, under ordinary circumstances, but in the case of the sewage of Belfast, and probably in that of other towns similarly situated, it is really necessary. At Belfast, at all events, one of the authors has shown that the growth in enormous quantities of the green sea-weed *Ulva latissima* and the resulting nuisance which occurs when it is washed ashore and putrefies—as happens each summer—is directly due to the fertilising properties of the sewage of the city, which is poured into the lough in an untreated condition.†

The experiments conducted by the authors consisted of: (1) A study of the changes which occur when potassium

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

† This used to be the case, but works for the purification of the sewage are being pushed on rapidly, and at the present time a considerable proportion is being purified.

nitrate is added to the effluent from a septic tank, and the speed with which they occur; (2) an investigation as regards the cause of these changes; (3) the action of pure cultures of specific micro-organisms in broth containing potassium nitrate.

1. *The Chemical Changes Occurring when Potassium Nitrate is added to the Effluent from a Septic Tank.*

The method of experiment consisted in completely filling two similar bottles (which were then tightly stoppered), one with the septic-tank effluent alone and the other with the same effluent *plus* an accurately measured volume of a strong standard solution of potassium nitrate (1 c.c. = 10 m.gs. nitric nitrogen). Allowing the two bottles so filled to remain at the temperature of the laboratory for a given interval of time, and then examining their contents quantitatively as regards (*a*) dissolved gases, (*b*) nitrates, (*c*) nitrites, (*d*) free and albumenoid ammonia.

Practically all the experiments (which were eight in number) were made with mixtures of potassium nitrate and septic-tank effluent containing 2·5 parts of nitric nitrogen per 100,000 in the case of the nitrated samples. The chief general conclusions arrived at were as follow:—

(1) Potassium nitrate (and no doubt any other nitrate likely to be produced in a sewage effluent) is decomposed by the septic-tank effluent, and the nitric nitrogen is evolved, sometimes entirely as free nitrogen, sometimes partly as nitric oxide. Nitrous oxide may also be formed, but the evidence on that point is not as yet conclusive. (Gayon and Dupetit found all three gases). The action seems to vary with different samples of septic-tank effluent, but in four of the eight experiments the theoretical quantity of nitrogen [corresponding with the added nitrate] was found either as free nitrogen alone or along with nitric oxide.

There is no evidence from the authors' experiments to show that any considerable quantity of these gases are produced from either the free ammonia or the organic nitrogen present in the septic-tank effluent.

(2) The general character of the change is that of a combustion, the oxygen of the nitrate eventually appearing either partly or entirely in the form of carbonic anhydride.

(3) In some of the experiments a little nitrite was produced, but in the majority none was found at their conclusion.

(4) The destruction of the nitrate occurs with remarkable rapidity, and in most of the experiments the whole of the added nitrate—equivalent to 2·5 parts of nitric nitrogen per 100,000 of mixture—was decomposed in twenty-four hours.

(5) In addition to the decomposition of the nitrate and evolution of carbonic anhydride the fermenting liquid experiences other changes.

There is always a *loss* of free ammonia, and as a rule a *gain* in albumenoid ammonia, but the former generally exceeds the latter. Thus in six experiments the average loss of free ammonia amounted to 0·266 part per 100,000, while the corresponding gain in albumenoid ammonia was only 0·166, or rather less than half the preceding figure.

It may also be mentioned that in two of the experiments marsh gas was found, not only in the septic-tank effluent, but also in the nitrated fluid, and it is somewhat remarkable that more of the gas was found in the latter than in the former.

Towards the end of the investigation the effects of aëration were studied. Parallel experiments were made, in one of which the septic-tank effluent was thoroughly aërated before mixing it with the nitrate, while in the other the same quantity of nitrate was added to the non-aërated effluent. In both experiments the whole of the nitrate was decomposed in twenty-four hours with evolution of the equivalent quantity of nitrogen gas. In the aërated sample no marsh gas was formed, but a considerable excess of carbonic anhydride was produced, the total volume per litre of fluid being 57·1 c.c., whereas the amount corresponding with the added nitrate *plus* the oxygen dissolved from the air was 49·8 + 5·53 = 55·33. In the non-aërated sample some marsh gas was formed, but considerably less carbonic anhydride.

The results obtained in this investigation suggest in part, at all events, an explanation of the production of free nitrogen in the "contact" beds commonly employed in the purification of sewage. These during the period they are in contact with air no doubt become charged with nitrates, and the latter are then destroyed when the beds are filled with sewage.

2. *Cause of the Decomposition of Nitrates when in Contact with a Putrefying Liquid.*

In order to ascertain whether the action was brought about entirely by the vital processes of micro-organisms, and was not due to enzymes excreted by them or to purely chemical changes, an apparatus was devised in which the septic-tank effluent was passed through a Chamberland filter and thence into a sterilised flask, from which it was drawn by a vacuum pump into two sterilised tubes of sufficient capacity, one of which contained a measured volume of the nitrate solution, and these tubes when filled were closed by pinch-cocks applied to indiarubber junctions. At the end of sixty-six hours analyses were made of the dissolved gases contained in the contents of both tubes, when it was found that they were practically identical, and that the nitrate had not been decomposed. The results of this experiment appear to be conclusive. The septic-tank effluent deprived of the micro-organisms which it contains has no action upon a nitrate. The decomposition of the latter must therefore be caused entirely by the vital processes of certain micro-organisms, and not by enzymic or chemical action.

3. *The Micro-organisms which Reduce Nitrates with Evolution of Nitrogen Gas or Oxides of Nitrogen.*

Gayon, Springer, Deherain, Maquenne, and others have isolated organisms from putrefying liquids which decompose nitrates with evolution of nitrogen or its oxides, but so far as can be judged from the printed abstracts of their work the identification of the species with known forms was either wanting or was incomplete. It occurred to the author that as the action is one of reduction it would be worth while to study the effects of those micro-organisms which are known to cause the evolution of hydrogen, such as *B. Amylobacter*, *B. Butyricus* (*Botkin*), *B. Lactis aërogenes*, and *B. Coli communis*, and as pure cultures of the latter happened to be available experiments were made with them.

An apparatus was constructed which permitted the introduction of pure cultures into a vessel filled with sterilised broth containing potassium nitrate from which the dissolved gases had been removed by boiling out in a vacuum.

With this apparatus experiments were first made on the action of pure cultures of *B. Coli communis* and *B. Lactis aërogenes* on broth alone. These were conducted at ordinary temperatures, and the fluid examined for dissolved gases as soon as a few bubbles of liberated gas had made their appearance. The dissolved gases were found (after removing carbonic anhydride) to consist entirely of hydrogen.

Experiments were then made with cultures of the same organisms and nitrated broth, and although they are not as yet completed the results so far obtained show that *B. Coli communis* liberates nitrogen from a nitrate in broth culture; *B. Lactis aërogenes* does not do so.

The authors desire to express their thanks to Professor Lorrain Smith, who supplied the pure cultures, and gave most valuable assistance and advice during the bacteriological part of the investigation.

Forthcoming Books.—*The Electrician* Printing and Publishing Company, Ltd., announce the early publication of the following:—Second Volume of Dr. J. A. Fleming's "Handbook of the Electrical Laboratory and Testing Room," 650 pages, fully illustrated, 14s. net. 1903 Revision of the "International Telegraph Convention and Telegraph and Telephone Service Regulations," 6s. net. New Edition of "Localisation of Faults in Electric Light Mains," by Mr. F. C. Raphael, 7s. 6d. net.

ON A METHOD FOR THE SEPARATION OF COBALT FROM NICKEL AND THE VOLUMETRIC DETERMINATION OF COBALT.*

By R. L. TAYLOR, F.I.C.

It has been long known that cobalt is precipitated from its solution as a higher oxide by the carbonates of barium, strontium, and calcium, in presence of chlorine or bromine. Long ago Rose proposed this as a means of separating cobalt from nickel, but he made the mistake of using a strongly acid solution. Of course the excess of acid was neutralised by the added carbonate, but the carbon dioxide thus produced retards enormously, if it does not altogether prevent, the complete precipitation of the cobalt. The author has found (*Memoirs of the Manchester Lit. and Phil. Soc.*, 1902, vol. xlvi., No. 11; and 1903, vol. xlvii., No. 12) that if a perfectly neutral and not too concentrated solution is used, cobalt is precipitated quantitatively as a black oxide in five or ten minutes by either barium or calcium carbonate in presence of bromine water. The two carbonates appear to act equally well, but the former is to be preferred if the subsequent removal of the added metal is desired. Whichever carbonate is used it should be in the precipitated form, and it is best made into a paste with water. If the liquid from which the cobalt is to be precipitated is acid, the acid may be neutralised by adding excess of the carbonate, but the liquid must then be well boiled to expel all the carbon dioxide, and then cooled before the bromine water is added. Not only does free carbonic acid prevent the precipitation of the cobalt, but zinc also considerably interferes with the reaction. A very small amount of that metal seriously retards the precipitation of the cobalt, and a large amount almost stops it altogether.

The author has ascertained the composition of the precipitated black oxide of cobalt by dissolving it in a mixture of hydrochloric acid and potassium iodide, and determining the amount of iodine liberated. It is fairly constant in composition, and approximates closely to the formulæ Co_9O_{14} and Co_7O_{11}. Which of these most correctly represents its composition he is unable to decide, but he suggests that its composition is sufficiently uniform to enable it to be used as a means for the volumetric determination of cobalt, by finding the amount of iodine which it liberates. The process has been tested by Mr. J. H. Davidson, B.Sc., in the assay of cobalt ores, and he finds it far more rapid than the processes generally in use, and at the same time quite sufficiently accurate for assay purposes.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

NOTICES OF BOOKS

Animal and Vegetable Fixed Oils, Fats, Butters, and Waxes. By C. R. Alder Wright, D.Sc. (Lond.), B.Sc. (Vict.), F.R.S. Second Edition. Edited and Partly Re-written by C. Ainsworth Mitchell, B.A. (Oxon.), F.I.C. London: Charles Griffin and Co., Ltd. 1903.

The second edition of this book has been revised and partly re-written for the purpose of making it suitable for use as an analytical text-book. Hence the addition of a great deal of matter describing methods of analysis and the detection and determination of adulterants, which considerably increases the value of the book and enlarges its scope. As in the original edition, the manufacture of candles, soaps, and other products receives a large amount of attention, and a very useful chapter is given on the analysis of soap. These chapters have all been brought well up to date, and considerably enlarged. The subjects dealt with in the volume include the general composition, nature, and sources of oils, butters, fats, and waxes, the physical and chemical properties of these substances, and the processes used for extracting, refining, and bleaching them. The data relating to the systematic description and classification of the oils appear to be most conveniently arranged for reference, and also to be very complete, considering the magnitude of the subject and the vast amount of literature dealing with it which has appeared in recent times.

Chemistry, Inorganic and Organic, with Experiments. By Charles Loudon Bloxam. Ninth Edition. Re-written and Revised by John Millar Thomson, LL.D., F.R.S., and Arthur G. Bloxam, F.I.C. London: J. and A. Churchill. 1903.

Some changes of importance have been made in the preparation of this edition of Bloxam's "Chemistry," notably among the illustrations, some of which are new, while many which appeared in earlier editions have been removed, and the arrangement also has been slightly altered. The general features of the book, however, remain the same, the method being strictly descriptive, though the constant reference to experiment makes it specially convenient for the use of the teacher in the preparation of lessons and lectures. As a work of reference it will still retain its place, especially where inorganic chemistry is concerned; the treatment of inorganic chemistry and organic in one volume has necessitated the condensation of the latter branch to an extent which seriously impairs its usefulness as a book to be put into the hands of the student. For conciseness sake many structural formulæ have been omitted in the belief that the reader may be trusted with the construction of them himself, but in all probability a large number of average students would rest content with endeavouring to commit to memory the formulæ as given, shirking the trouble necessary for the building up of the structural formulæ, and thus failing to get the best possible grasp of the principles involved. This condensation also has led to some omissions; for example, the important synthetic method known as Perkin's reaction for the preparation of cinnamic acid is by no means given the attention it deserves, and is not even mentioned by its familiar name, and in dealing with Reimer's reaction the question of the separation of the ortho- and para-compounds is not even touched upon. The sections on some of the useful applications of the principles of organic chemistry are, however, particularly full and good for a work of this nature.

CORRESPONDENCE.

PATENTS IN HOLLAND.

To the Editor of the Chemical News.

Sir,—Holland has long been almost the only highly civilised country in the world which does not grant patents of invention. We have received information, however, from our agents that the Dutch Government are now preparing a Patent Law, and its early presentation to Parliament was mentioned in the Queen's Speech. Holland is a member of the Union for the Protection of Industrial Property, consisting of nearly all the principal countries of the world, except Austria, Hungary, Russia, Persia, China, and Turkey, and each country in the Union has pledged itself to a large extent of reciprocity in connection with patents and trade marks.—We are, &c.,

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6, Lord Street, Liverpool,
September 23, 1903.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 8, August 24, 1903.

Piles consisting of Different Liquids with Identical Metallic Electrodes.—M. Berthelot.—The author has already shown that certain relations exist between the electromotive forces of the elements of piles with different metallic electrodes. He proceeds further with this research, and performs experiments on the elements of piles with different liquids, but terminated by identical electrodes. He then compares the observed results with those of theory. When the electrodes are identical, in principle there is no difference of potential in a cell composed of a single liquid, but only in elements composed of 2, 3, 4, 5, &c., separated liquids of different composition. He now examines only the elements in which there are two distinct and terminal liquids—that is to say, in contact with the metallic electrodes, which are identical. He operates with three metals—zinc, copper, and platinum. All the solutions possess equivalent concentrations—1 mol. = 5 litres for monovalent bodies; 1 mol. = 10 litres for divalent bodies.

Nos. 9 and 10.

These two numbers contain no chemical matter.

MISCELLANEOUS.

Peroxide of Cerium.—E. Baur.—By shaking up cerous sulphate in solution in carbonate of potassium liquor, in contact with air, we obtain an oxidation corresponding to the transformation of 83·6 per cent of cerium to the perceric state. In the presence of a body such as arsenite of soda (compare Manchot, *Zeit. Anorg. Chem.*, vol. xxvii., p. 420; *Bull. Soc. Chim.*, vol. xxviii., p. 406), this latter becomes oxidised, and the total quantity of fixed oxygen corresponds in a manner approaching the primary formation of the peroxide. The action of a cerous salt on a mixture of iodide of potassium and peroxide of hydrogen gives rise to the liberation of iodine, which is not opposed to the formation of a peroxide, but which, all the same, does not prove its existence. When we treat the salt described by Job (*Ann. de Chim.*, [7], vol. xx., p. 253) with sulphuric acid, oxygen is given off; apparently the decomposition is according to the following equation :—

$$2CeO_3 + 4SO_4H_2 = 2(SO_4)_2Ce + 2H_2O + 2H_2O_2 = (SO_4)_3Ce_2 + O_2 + H_2O_2 + 2H_2O.$$

The amount of active oxygen liberated, which theoretically should be double that remaining in solution in the form of H_2O_2, is in reality greater, apparently on account of a partial and spontaneous decomposition of the peroxide of hydrogen.—*Zeit. Anorg. Ch.*, vol. xxx., p. 251.

Oxalo-niobic Acid.—Franz Russ.—The raw material used was colombite. The author first passes in review the different methods of treatment for the preparation of niobic acid. Oxalo-niobate of potassium is obtained by fusing together in a platinum crucible 16 grms. of fused niobic acid with 24·7 grms. of carbonate of potassium. After fusion, the mass is taken up with water, and the insoluble residue (about 0·185 grm. in weight) is separated; the solution is mixed with another solution containing 45·1 grms. of oxalic acid. The return is about 50 grms. The salt, which has the formula $Nb_2O_5.3K_2O.6C_2O_3.4H_2O$, is crystalline, and occurs in spheroidal agglomerations. The sodium salt, which is more difficult to obtain, contains $8H_2O$, the ammonium salt $3H_2O$, that of rubidium $4H_2O$. All the attempts made for the preparation of the alkaline salts of the type $2Nb(C_2O_4K)_5 = Nb_2O_5.5K_2O.10C_2O_3$ were failures. Solutions of niobic and of oxalic acids furnish crystals of which the composition varies considerably. Under certain experimental conditions, the author obtained by analysis figures comparable with those required by the formulæ $3Nb_2O_5.2C_2O_3.20H_2O$, $Nb_2O_5.C_2O_3.3H_2O$, and $Nb_2O_5.C_2O_3.4H_2O$. In the presence of a small quantity of oxalic acid there is a tendency towards the formation of the body $Nb_2O_5.C_2O_3$; in the presence of an excess of this acid the tendency is to form $Nb(C_2O_4H)_5$, from which we get the formation of the complex mixtures like $Nb_2O_5.5C_2O_3.21H_2O$. An aqueous solution of oxalo-niobate of potassium, $Nb_2O_5.3K_2O.6C_2O_3.4H_2O$, at 2 per cent, precipitates the alkaline earthy salts and a large number of the metallic salts, but the salts of manganese, zinc, mercury (Hg") are not precipitated. The decomposition of the binoxalate of barium by an excess of niobic acid, leads to the formation of the salt $Nb_2O_5.5BaO.10C_2O_3.20H_2O$. The action of dry chlorine gas transforms the oxalo-niobate of potassium into Nb_2O_5 and KCl, even at a temperature near to 100°. Tetrachloride of carbon decomposes it in the same manner, but the reaction only commences at about 200°. With hydrochloric acid the decomposition takes place at a red heat. Sulphide of carbon gives sulphides at a temperature below red heat. The author has made some measurements of the conductivity of solutions of alkaline oxalo-niobates (K, Na, Am, Rb). The separation of tantalum and niobium by means of the complex oxalates cannot be effected.—*Zeit. Anorg. Ch.*, vol. xxxi., p. 42.

TO CORRESPONDENTS.

G. W Thornhill.—The question is outside the scope of our paper. Apply to some medical journal.

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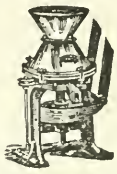

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2290.

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 177).

Chapter III. (*continued*).

Proportion of β-Rays in the Radiation of Radium.

As I have already mentioned, the proportion of β-rays increases with increase of distance from the source of radiation. These rays never occur alone, and for great distances the presence of γ-rays is always discernible. The presence of very penetrating, undeflected rays in the radiation of radium was first observed by M. Villard. These rays constitute only a small portion of the radiation measured by the electrical method, and their presence escaped our notice in our first experiments, so that we believed falsely that the radiation at great distances contained only rays capable of deflection.

The following are the numerical results obtained with experiments made by the electrical method with an apparatus similar to that of Fig. 5. The radium was only separated from the condenser by the surrounding air. I shall indicate by the letter *d* the distance from the source of radiation to the condenser. The numbers of the second line represent the current subsisting when the magnetic field is acting, supposing the current obtained with no field equal to 100 for each distance. These numbers may be considered as giving the percentage of the total α- and γ-rays, the deflection of the α-rays having been scarcely observable with the conditions employed.

At great distances there are no α-rays, and the undeflected radiation is therefore of the γ kind only.

Experiments made at short distances:—

d, in centimetres	3·4	5·1	6·0	6·5
Percentage of undeflected rays	74	56	33	11

Experiments made at long distances with a product considerably more active than that which was used for the preceding series:—

d, in centimetres	14	30	53	80	98	
Percentage of undeflected rays	12	14	17	14	16	
d	124	157				
Percentage of undeflected rays	14	11				

It is thus evident that after a certain distance the proportion of undeflected rays in the radiation is approximately constant. These rays probably all belong to the γ species.

The following is another series of experiments in which the radium was enclosed in a very narrow glass tube, placed below the condenser and parallel to the plates. The rays emitted traversed a certain thickness of glass and air before entering the condenser:—

d, in centimetres ..	2·5	3·3	4·1	5·9	7·5	9·6	11·3
Percentage of rays not deflected ..	33	33	21	16	14	10	9
d	13·9	17·2					
Percentage rays not deflected	9	10					

As in the preceding experiments, the number of the second line approximate to a constant value, when the distance *d* increases, but the limit is reached for smaller distances than in the preceding series, because the α-rays have been more completely absorbed by the glass than the β- and γ-rays.

The following experiment shows that a thin sheet of aluminium (0·01 m.m. thick) absorbs principally α-rays. The product being placed 5 c.m. from the condenser, the proportion of rays other than β, when the magnetic field is acting, is about 71 per cent. When the same substance is covered with the sheet of aluminium, the distance remaining the same, the radiation transmitted is found to be almost totally deflected by the magnetic field, the α-rays having been absorbed by the aluminium. The same result is obtained when paper is used as the absorbing screen.

The greatest part of the radiation of radium consists of α-rays, which are probably emitted principally by the superficial layer of the radiating matter. When the thickness of the layer of radiating matter is varied, the intensity of the current increases with this thickness; the increase is not proportional to the thickness for the whole of the radiation; it is, moreover, more considerable for the β-rays than for the α-rays, so that the proportion of β-rays increases with the thickness of the active layer. The source of radiation being placed at a distance of 5 c.m. from the condenser, it is found that for a thickness equal to 0·4 m.m. of the active layer, the total radiation is given by the number 28, and the proportion of the β-rays is 29 per cent. By making the layer 2 m.m. thick, *i.e.*, five times as thick, a total radiation equal to 102, and a proportion of β-rays equal to 45 per cent are obtained. The total radiation which exists at this distance has therefore been increased in the ratio of 3·6, and the β-radiation has become five times as strong.

The preceding experiments were made by the electrical method. When the radiographic method is used, certain results seem to be in contradiction with what precedes. In the experiments of M. Villard, a beam of radium rays, subjected to the action of the magnetic field, was received on to a pile of photographic plates. The undeflected and penetrating γ-beam passed through all the plates, leaving its trace on each. The deflected β-beam produced an impression on the first plate only. This beam appeared therefore to contain no rays of great penetration.

On the contrary, in our experiments a beam which is propagated in the air contains at the greatest distances accessible to observation about 9/10 of β-rays, and the same is the case when the source of radiation is enclosed in a little sealed glass vessel. In M. Villard's experiments, these deflected and penetrating β-rays did not affect the photographic plates beyond the first, because they are to a great extent diffused in all directions by the first solid obstacle encountered, and no longer form a beam. In our experiments the rays given off by radium and transmitted through the glass of the vessel were also probably scattered by the glass, but the vessel being very small would itself act as a source of β-rays at its surface, and we were able to follow the course of the latter to a great distance from the vessel.

The cathode rays of Crookes tubes can only traverse very thin screens (aluminium screens of 0·01 m.m. thickness). A beam of rays striking the screen normally is scattered in all directions; but the diffusion becomes less with diminishing thickness of the screen, and for very thin screens the emerging beam is practically the prolongation of the incident beam.

The deflected β-rays of radium behave in a similar manner, but the transmitted beam experiences, for the same thickness of screen, a much slighter modification. According to the experiments of M. Becquerel, the very readily deflected β-rays of radium (those with a relatively small velocity) are powerfully scattered by an aluminium screen of thickness 0·1 m.m.; but the penetrating and less deflected rays (rays of the cathode kind of great velocity) pass through this screen without being sensibly diffused, whatever be the inclination of the screen to the direction of the beam. The β-rays of great velocity penetrate without diffusion a much greater thickness of paraffin (several centimetres), and in this the curvature of the beam produced by the magnetic field can be traced. The thicker the

* Thesis presented to the Faculté des Sciences de Paris.

screen, and the more absorbent the material of which it is composed, the greater is the modification of the deflected primitive beam, because, with increasing thickness of screen, diffusion occurs progressively among fresh groups of rays of increasing penetration.

The β-rays of radium experience a diffusion in passing through the air, which is very marked for readily deflected rays, but which is much slighter than that produced by equal thicknesses of solid substances. For this reason, the β-rays traverse long distances in the air.

Penetrating Power of the Radiation of Radio-active Bodies.

Since the beginning of the researches on radio-active bodies, investigations of the absorption produced by different screens upon the rays given off by these bodies have been carried on. In a previous paper on this subject I gave figures (quoted at the beginning of this work) representing the penetrating power of uranium and thorium rays. Mr. Rutherford has made a special study of the radiation of uranium, and proved it to be heterogeneous. Mr. Owens has arrived at the same results for thorium rays. When the discovery of strongly radio-active bodies immediately followed upon this, the penetrating power of their rays was also studied by various physicists (Becquerel, Meyer and von Schweidler, Curie, Rutherford). The first observations brought to light the complexity of the radiation, which seems to be a general phenomenon, and common to the radio-active bodies. In them we have sources which give rise to a variety of radiations, each of which has a power of penetration proper to itself.

Radio-active bodies emit rays which are propagated both in the air and *in vacuo*. The propagation is rectilinear; this fact is proved by the distinctness and shape of the shadows formed by interposing bodies opaque to the radiation between the source and the sensitive plate or fluorescent screen which serves as receiver, the source being of small magnitude in comparison with its distance from the receiver. Various experiments demonstrating the rectilinear propagation of uranium, radium, and polonium rays have been made by M. Becquerel.

It is interesting to know the distance that rays can travel in air. We have found that radium emits rays which can be detected in the air at a distance of several metres from the source. In certain of our electrical determinations, the action of the source upon the air of the condenser made itself felt at a distance of between 2 and 3 metres. We have also obtained fluorescent effects and radiographic impressions at similar distances. The experiments are not easily carried out, except with very intense radio-active sources, because, independently of the absorption by the air, the action upon a given receiver varies inversely as the square of the distance from a source of small dimensions. This radiation, which travels a long distance in the case of radium, comprises rays of the cathode kind and rays which are undeflected; however, the deflected rays predominate, according to the results of the experiments already mentioned. The greater part of the radiation (α-rays) is, on the contrary, limited in air to a distance of about 7 c.m. from the source.

I made several experiments with radium enclosed in a little glass vessel. The rays emerging from the vessel, after traversing a certain space of air, were received in a condenser, which served to measure their ionising capacity by the usual electrical method. The distance, d, from the source to the condenser was varied, and the current of saturation, i, obtained in the condenser was measured. The following are the results of one of the series of determinations. (See next column).

After a certain distance, the intensity of radiation varies inversely as the square of the distance from the condenser.

The radiation of polonium is only propagated in air to a distance of a few centimetres (4 to 6 c.m.) from the source of radiation.

In the case of the absorption of radiations by solid screens, we find another fundamental difference between

d, c.m.	i.	$(i \times d^2) \times 10^{-3}$.
10	127	13
20	38	15
30	17·4	16
40	10·5	17
50	6·9	17
60	4·7	17
70	3·8	19
100	1·65	17

radium and polonium. Radium emits rays capable of penetrating great thicknesses of solid matter, *e.g.*, several centimetres of lead or of glass. The rays which have passed through a great thickness of a solid body are extremely penetrating, and it is practically impossible to absorb them entirely by any material whatever. But these rays form only a small fraction of the total radiation, the greater part of which is absorbed by a slight thickness of solid matter.

Polonium emits rays which are readily absorbed, and which can only pass through extremely thin screens.

The following are figures showing the absorption produced by an aluminium lamina of thickness 0·01 m.m. This lamina was placed above and almost in contact with the substance. The direct radiation and that transmitted by the aluminium were measured by the electrical method (apparatus of Fig. 1); the current of saturation was practically obtained in every case. I have represented the activity of the radiating body by a, that of uranium being unity.

	a.	Fraction of radiation transmitted.
Chloride of barium and radium	57	0·32
Bromide ,, ,,	43	0·30
Chloride ,, ,,	1200	0·30
Sulphate ,, ,,	5000	0·29
,, ,, ,,	10,000	0·32
Metallic bismuth and polonium	—	0·22
Compounds of uranium ..	—	0·20
Compounds of thorium in a thin layer	—	0·38

We see that radium compounds of different nature and activity give very similar results, as I have already pointed out in the case of uranium and thorium compounds at the beginning of this work. We see also that, taking into account the whole of the radiation, and with a given absorbent screen, the different radio-active bodies can be arranged in the following decreasing order of penetrating power:—Thorium, radium, polonium, uranium.

These results are similar to those which have been published by Mr. Rutherford.

Mr. Rutherford also finds that the order is the same when air is the absorbent substance. But it is probable that this order has no absolute value, and would not be maintained independently of the nature and thickness of the screen. Experiment shows, indeed, that the law of absorption is very different for polonium and radium, and that, for the latter, the absorption of the rays of each of the three groups must be considered separately.

(To be continued).

Action of Mixed Organo-magnesium Compounds on Bodies with a Nitrated Function.—Louis Meunier.—The author has examined the action of some of these bodies, such as the ethereal solution of ethyl-iodide of magnesium, on ammonia, on aniline, and on diazoamidobenzene; and of ethyl-bromide of magnesium on phenylhydrazine. The above reactions enabled him to obtain the methanic carbides from the iodides or bromides of the corresponding alcohols.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 8.

ESTIMATION OF ARSENIC IN SEA-WATER, SEA-SALT, ROCK-SALT, MINERAL WATERS, &c., AND IN SOME OF THE ORDINARY REAGENTS.

By ARMAND GAUTIER.

It has been known for some time that sea-water contains a small proportion of arsenic. I have shown that it is partly in solution and partly organic, contained in the constituents of *plankton*, especially in the microscopic algæ, in which it accompanies the iodine (*Comptes Rendus*, vol. cxxxv., p. 833); but, up to the present, the difficulty of collecting the whole of these traces of arsenic in the presence of a large quantity of chlorides and other salts has made any exact determination of this element in salt waters impossible.

The new method I have described recently (see Chemical News, vol. lxxxviii., p. 177) enables us, on the contrary, to estimate the arsenic in sea-water, sea-salt, and rock-salt with the greatest ease.

For the purpose of my research on physiological arsenic, I have been obliged to estimate it also in distilled water and in the reagents generally met with in legal medicine.

Sea-water, Salt Springs.—In the sea-water from the Atlantic (coast of Brittany) I attempted to estimate the arsenic in its three forms—*mineral*, *organic*, and *organised*.

The water, filtered through biscuit porcelain, was treated with 10 c.c. per litre of ferric sulphate free from arsenic (this ferric solution contained 30 grms. of Fe_2O_3 per litre), boiled, saturated with ammonia, and filtered. The mineral arsenic was estimated, as has been described (*loc. cit.*), by dissolving the ferric precipitate in dilute sulphuric acid, and transferring directly to the Marsh apparatus. For the organic arsenic, the solution from which the above ferric precipitate was obtained was treated, after filtration, with 70 c.c. of pure nitric acid, and distilled to dryness on a sand-bath in a glass retort fitted with a condenser terminating in a Will and Varrentrap tube containing a warm solution of pure potash, the whole being connected together with ground joints. It was ascertained that under these conditions the glass did not give up any perceptible amount of arsenic to the acid (less than 0·0003 m.grm.). The non-condensed acid fumes and the chloride passes bubble by bubble through the purified potash (this contained 0·0044 m.grm. of As per 100 c.c., and 0·0006 m.grm. for the amount used) destined to collect and destroy the fumes of chloride of arsenic which might be produced. After complete desiccation and gentle calcination of the dry residue in the retort, the acid liquor distilled and the alkaline solution in the tubes were mixed, neutralised, treated with 10 c.c. of ferric solution, and boiled, &c., as before.

After making all corrections for traces of arsenic introduced, the following results were obtained:—

A. *Sea-water taken 30 Kilometres off the Coast of Brittany at 5 Metres below the Surface.*

	M.grms. per litre of water.
Mineral arsenic	0·009
Organic „	0·0008 (about)
Organised „	Not weighable in 1 litre.

B. *The same Sea-water.*

Total arsenic	0·010

The following determinations are of interest, having been made on samples of water from the Atlantic from the neigbourhood of the Azores, in the same vertical line but at different depths. These samples were collected with all possible precautions by His Highness the Prince of Monaco, to whom I offer my sincere thanks:—

Water from the Atlantic (Azores).

	Depth. Metres.	Arsenic per litre. M.grms.
S. 1394	10	0·025
—	1335	0·016
S. 1427 ($t = 2·7°$)	5943 (6 or 8 metres from the bottom) ..	0·080

Thus it appears that, in the neighbourhood of volcanic regions, arsenic is abundant, especially at great depths. We shall see later on that arsenic comes principally from volcanic action.

The waters from salt springs are all more or less arsenical, especially ferruginous waters and those containing sodic chloride. This new method enables us to estimate the arsenic present with great precision. Chloride of sodium does not interfere at all with the carrying down of this metalloid by the ferric salt, which becomes insoluble when heated. As an example, I will give the estimation I made on the salt water from Misserey, near Besançon. This water, which was almost saturated with salt (it contained 326 grms. per litre) gave—

Arsenic per litre .. .. 0·010 m.grm.

This is the same amount that is contained in the water at the entrance to the English Channel at the surface.

Sea-salt, Rock-salt.—It appeared to me to be probable that sea-salt from sea-water rich in arsenic might contain a sensible proportion of this element. This was confirmed by the following analyses:—

Origin.	M.grms of arsenic per 100 grms. of salt.
Fine white salt—	
Coast of Brittany	0·003
Sands of Olonne..	0·001
Grey kitchen salt—	
Sands of Olonne (Atlantic):—Soluble, 0·035; insoluble, 0·010	0·045
Salt said to be English*—	
Bought at Potin's, Paris	0·015
Rock salt—	
Stassfurth (beautiful, transparent)	0·0025
St. Nicholas. near Nancy:—Soluble, 0·009; insoluble, 0·005	0·014
Mountain of salt at Djebel-Amour (South Oran)	0·005
Chloride of sodium, fused at a red heat.. ..	0·030
Chloride of sodium, collected in a volcanic fissure on Vesuvius	0·175

* This salt was very fine and opaque, and appeared to be mixed with a small proportion of spices.

Thus, chloride of sodium always contains arsenic, especially if it is of direct volcanic origin, as shown by the last sample.

We get further information also from these analyses. Of all the common kinds of salt, the grey kitchen salt is the richest in arsenic. It constitutes one of the principal sources from which we draw our daily necessary supply of arsenic, which certain of our organs seize upon with such avidity.

From the medico-legal point of view, due regard must be given to the continuous introduction of arsenic by means of kitchen salt. But it must be remarked that the quantities absorbed by this means are minimal (about a decimilligrm. per month). Above all, it must not be forgotten that I have proved that the liver, the blood, the stomach, the muscles, &c., of mammals do not contain arsenic in their normal states, or at most an amount lower than $\frac{1}{100}$th of a milligrm. per 100 grms. after deducting that due to the reagents, especially the sulphuretted hydrogen.

Various Reactions.—Finally, I wished to determine, by means of my new method, the amounts of arsenic that the

supposed pure reagents had introduced into the estimations made by my old method. The following results were obtained :—

	Arsenic per litre. M.grm.
Water, distilled in a tinned copper retort (treated with 1 grm. CO_3Na_2 per litre)	0·0007
Water, distilled in a glass retort with 1 per cent of pure CO_3NaH	0·0011
	Per 100 c.c.
Pure commercial ammonia	0·0010
Ammonia made from sulphate of ammonia free from arsenic, and caustic soda reputed pure	0·0033
	Per 100 grms.
Pure commercial bicarbonate of soda	0·016
Pure commercial nitre	0·0015
Reputed pure sulphate of potassium	0·006
The same, purified by $(SO_4)_3Fe_2$, containing 30 grms. Fe_2O_3 per litre	0·0000
	Per 30 grms. Fe_2O_3.
Purified ferric sulphate	0·0004
	Per 100 grms.
Specially purified nitric acid	0·00023
	Per 100 c.c.
Concentrated aqueous solution of sulphurous acid gas	0·005
Sulphuretted hydrogen, obtained from ordinary FeS and HCl, and washed carefully with acids and with water	A considerable quantity.
The same sulphuretted hydrogen, purified	0·0008*
	In 30 grms.
Pure zinc	0·0000

* The whole of this arsenic was carried by a current of bubbles of medium velocity during two hours through pure nitric acid at 80°, placed in a long-necked flask, not giving arsenic. In a future paper I will describe the method of purifying sulphuretted hydrogen.

It will be observed that most of the so-called pure reagents used habitually in the detection of arsenic by the old method, such as the distilled water, the nitric and sulphuric acids, the bisulphites, the ammonia and its carbonate, and *especially* the sulphuretted hydrogen, contain a trace—and this latter gas a considerable quantity—of arsenic. The amount introduced by my new method is nil, but the same is not the case when we have recourse to the old ones. It is quite possible, by using impure sulphuretted hydrogen, to obtain more than 0·001 grm. of arsenic.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 16.

ON THE RESOLUTION OF ELEMENTARY SUBSTANCES INTO THEIR ULTIMATES, AND ON THE SPONTANEOUS MOLECULAR ACTIVITY OF RADIUM.*

By HENRY WILDE, D.Sc., F.R.S.

The author refers to several of his papers published by the Society on the genesis of elementary substances, and on the multiple proportions of their atomic weights, wherein certain gaps appeared in the several series in his tables which have since been filled up by scandium, germanium, helium, argon, neon, krypton, and xenon. The remarkable properties of radium bring about further realisations of the predictions made in the author's earlier papers. The series H_2n has long been remarkable for the property of phosphorescence which some of its lower members possess above those of other series of elements. Radium has been shown by its discoverers, M. and Mdme. Curie, to be the next higher member of the calcium, strontium, and barium series of alkaline earth metals, and that its halogen compounds are permanently self-luminous. The author had previously indicated the remarkable interruption in the regularity of his multiple series H_2n through the absence of elements of atomic weights 160 and 184 respectively. As there is only one place vacant higher in this series for an analogue of calcium, strontium, and barium, radium is identified by the author as the tenth elementary condensation of H_2n, with an atomic weight of 184 and a specific gravity of 4·8, as shown in his tables. The author has shown in former papers that helium was the unknown typical molecule of the same series, with an atomic weight of 2, and had previously indicated the probability of the resolution of the higher members of each series into their elementary typical molecules. The production of helium from radium by Professors Rutherford, Soddy, and Ramsay confirms the author's prevision in the case of the series H_2n, and this result may lead to the resolution of the higher members of other series into their ultimates.

The discovery of MM. Curie and Laborde of the spontaneous molecular activity of radium also confirms the views expressed by the author in the course of his lecture delivered before the Society in 1902, with reference to the spontaneous molecular and molar activity of endothermic substances.

* Abstract of a Paper read before the Manchester Literary and Philosophical Society, October 6, 1903.

DUTY-FREE ALCOHOL FOR SCIENTIFIC RESEARCH.*

The Committe appointed at the Glasgow meeting in 1901 were unable to report in 1902, as they were at the time of the Belfast meeting in the midst of their negotiations with the Board of Inland Revenue.

After a preliminary meeting and correspondence in the winter of 1901-2 the Committee received information that the Government were willing to adopt a clause in the Budget Bill of 1902 which would permit the use of duty-free alcohol under conditions to be laid down by the Board of Inland Revenue. When the Budget Bill was passed a deputation from the Committee waited on the Chairman of the Board, and after full discussion the Committee agree to confine their application at the present time to the use of duty-free alcohol (ethyl and methyl) and of alcoholic derivatives for the purposes of research work and higher teaching in the laboratories of universities, colleges, and public institutions.

At the request of the Chairman of the Board of Inland Revenue the Committee drew up the following statement :—

"*To the Chairman of the Board of Inland Revenue.*

"August 6, 1902.

"Sir,—At the meeting of the British Association held at Glasgow last year a Committee was appointed to approach the Inland Revenue Commissioners to urge the desirability of securing the use of pure alcohol duty-free for the purposes of scientific research.

"It was pointed out at the Glasgow meeting that the low price of pure alcohol and its derivatives on the Continent and the high duty payable in the United Kingdom, severely handicapped research workers here in chemistry, physiology, and pathology, and to a smaller extent in zoology and botany. In the recent debates on the Budget Bill this disadvantage was recognised, and steps were taken with a view to remedy the evil.

"In the United States, where alcohol is taxed, permits are granted to scientific institutions of certain rank enabling them to obtain duty-free alcohol for use in their laboratories. The conditions under which these permits are granted by the United States Treasury have been obtained by this

* Report of the Committee, consisting of Sir H. Roscoe (Chairman), Prof. H. B. Dixon (Secretary) Sir Michael Foster, Sir A. W. Rücker, Dr. T. E. Thorpe, Prof. W. H. Perkin, and Prof. W. D. Halliburton. Read before the British Association (Section B), Southport Meeting, 1903.

Committee. A copy of these regulations was placed in your hands at the interview you were good enough to grant on the 9th inst to members of this Committee.

"In accordance with your request we have obtained some statistics as to the amount of alcohol (and its derivatives) used in English laboratories for higher teaching and research work. It has not been possible to obtain complete details, but the following figures, which are the average number of *gallons* used per annum during the last three years in the laboratories at Cambridge, at Owens College, and the Yorkshire College, may be taken as typical :—

	Absolute ethyl alcohol.	Rectified spirit.	Absolute methyl alcohol.	Ethyl ether.	Methylated spirit.
I. *Cambridge (University and College Laboratories).*					
Chemical Laboratories..	30	30	—	60	
Pathological ,, ..	15	—	—	10	
Physiological ,, ..	10	10	—	10	500
Zoological and Botanical Laboratories	20	—	—	—	
II. *Owens College.*					
Chemical Laboratories..	50	—	20	80	100
Pathological ,, ..	15	—	—	5	5
Physiological ,, ..	5	—	—	—	25
Zoological and Botanical Laboratories	5	—	—	1	120
III. *Yorkshire College.*					
Chemical Laboratories..	15	—	12	25	50
Medical Department ..	—	—	—	—	150

It should be pointed out that if pure alcohol could be obtained duty-free more would be used in scientific work instead of the methylated spirit now used whenever possible.

"From the table given it will be seen that the chief demand in scientific laboratories is for pure ethyl alcohol and pure ethyl ether. But other alcohols (*e.g.*, methyl alcohol) and other derivatives of alcohols (*e.g.*, methyl and ethyl iodides) and ethereal salts (*e.g.*, malonic ether) are largely used in organic chemistry. These reagents are at present mainly imported from Germany, and pay duty to the Customs. There is therefore a desire that such ethereal compounds might be imported duty-free for scientific use.

"In the request that we now make for the use of duty-free ethyl alcohol and its derivatives, for the purpose of higher teaching and research, we would point out that the alcohol (or other reagent) is destroyed or contaminated beyond recovery by the use to which it is put, and such destruction or contamination could be certified by the director of the laboratory.

"In the opinion of the Committee there would be no difficulty in arranging for one distributing station in each university centre to supply the several laboratories of that centre."

On October 22 the Committee received from the Board a draft of the suggested regulations under which it was proposed to authorise the issue, in accordance with section 8 of the Finance Act, 1902, of pure spirit duty-free for purposes of scientific research and education. The Board asked for observations on the proposed regulations.

The Committee had copies of these proposed regulations sent to the directors of the chief laboratories in the country, with a request that they would forward any suggestions they might wish to make to the Committee. After considering the suggestions sent in, the Committee submitted their observations to the Board, who adopted the alterations suggested, and informed the Committee that *methyl alcohol* might be obtained under the same regulations.

The Committee, with the permission of the Board of Inland Revenue, published the regulations in the *Times* and other newspapers with the accompanying explanatory letter :—

"Duty free Alcohol for Research.

"*To the Editor of the Times.*

"December 15, 1902.

"Sir,—It has long been felt by scientific workers in this country that a serious drawback to the prosecution of research lies in the fact that the full and very heavy duty has to be paid on pure alcohol, as distinguished from methylated spirit, largely used in scientific laboratories where higher teaching and research are carried on. And this appeared to be a hardship in the first place because the alcohol thus used is either destroyed or rendered useless for potable purposes, and in the second place because no such duty is paid in Germany, France, or the United States, and thus the British is heavily handicapped as against the foreign worker.

"At the meeting of the British Association held last year in Glasgow, a Committee was appointed with instructions to approach the Board of Inland Revenue with the object of endeavouring to secure the removal of this grievance—a grievance which was recognised by Government in the Budget Bill of this year. We are now glad to report that the Board has met our suggestions in the fairest possible manner with an obvious desire to extend facilities for scientific research in the direction indicated, as a perusal of the regulations which we enclose will show.

"The Secretary to the Board of Inland Revenue informs us that pure 'methyl alcohol,' also much used in chemical research, may be obtained under the same regulations, and should smaller quantities of methyl alcohol be required than the minimum permitted in the case of ethyl alcohol, the Board will consider special applications to that effect. —We are, &c.,

"H. E. Roscoe, Chairman.

"H. B. Dixon, Secretary to the Committee."

(Enclosure).

Regulations for the Use of Duty-free Spirit at Universities, Colleges, &c.

1. An application must be made by the governing body or their representatives, stating the situation of the particular university, college, or public institution for research or teaching, the number of the laboratories therein, the purpose or purposes to which the spirits are to be applied, the bulk quantity likely to be required in the course of a year, and, if it amounts to fifty gallons or upwards, the name or names of one or more sureties, or a guarantee society to join in a bond that the spirits will be used solely for the purpose requested and at the place specified.

2. The spirits received at any one institution must only be used in the laboratories of that institution, and must not be distributed for use in the laboratories of any other institution, or used for any other purpose than those authorised.

3. Only plain British spirits or unsweetened foreign spirits of not less than 50 degrees over-proof (*i.e.*, containing not less than 80 per cent by weight of absolute alcohol) may be received duty-free, and the differential duty must be paid on the foreign spirits.

4. The spirits must be received under bond either from a distillery or from an Excise or Customs general warehouse, and (except with special permission) in quantities of not less than nine bulk gallons at a time. They will be obtainable only on presentation of a requisition signed by the proper supervisor.

5. On the arrival of the spirits at the institution the proper revenue officer should be informed, and the vessels, casks, or packages containing them are not to be opened until he has taken an account of the spirits.

6. The stock of spirits in each institution must be kept under lock in a special compartment under the control of a professor or some responsible officer of the university, college, or institution.

7. The spirits received by the responsible officer of the

institution may be distributed by him undiluted to any of the laboratories on the same premises.

8. No distribution of spirits may be made from the receiving laboratory to other laboratories which are not within the same premises.

9. A stock-book must be provided and kept at the receiving laboratory, in which is to be entered on the debit side an account of the bulk and proof gallons of spirits received with the date of receipt, and on the credit side an account of the bulk and proof gallons distributed to the other laboratories. A stock-book must also be kept at each other laboratory, in which must be entered on the day of receipt an account of the bulk and proof gallons of spirits received from the receiving laboratory. These books must be open at all times to the inspection of the revenue officer, and he will be at liberty to make any extract from them which he may consider necessary.

10. The quantity of spirits in stock at any one time must not exceed half the estimated quantity required in a year where that quantity amounts to 20 gallons or upwards.

11. Any contravention of the regulations may involve the withdrawal of the Board's authority to use duty-free spirits.

12. It must be understood that the Board of Inland Revenue reserve to themselves full discretion to withhold permission for the use of duty-free spirit in any case in which the circumstances may not seem to them to be such as to warrant the grant of it.

Note.—"Proof spirit" is defined by law to be such as at the temperature of 51 degrees Fahrenheit shall weigh 12—13 of an equal measure of distilled water. Taking water at 51 degrees Fahrenheit as unity, the specific gravity of "proof spirit" at 51 degrees Fahrenheit is 0·92308. When such spirit is raised to the more usual temperature of 60 degrees Fahrenheit, the specific gravity is 0·91984. To calculate the quantity of spirits at proof in a given quantity of spirit over or under proof strength, multiply the quantity of spirit by the number of degrees of strength of the spirit, and divide the product by 100. The number of degrees of strength of any spirit is 100 plus the number of degrees overproof, or minus the number of degrees underproof.

Example:—

19·8 gallons of spirits at 64·5 overproof
100 + 64·5 = 164·5 proof strength.
164·5 × 19·8 ÷ 100 = 32·571
taken as 32·5 gallons at proof.

ON THE

POSSIBILITY OF MAKING SPECIAL REPORTS MORE AVAILABLE THAN AT PRESENT.*

The Committee recommend:—

1. That at the close of each annual meeting of the Sectional Committee shall request its secretaries to compile a list of the Special Reports, other than those of Standing Committees, which have been presented to the Section during the previous five years, and which have been published *in extenso*, this list (see Appendix) to include those Reports of the character specified which have been presented at the annual meeting just terminated.

2. That the secretaries of the Sectional Committee be requested to forward copies of the list to the secretaries of the Chemical Societies of London and Berlin, with the suggestion that the councils of these bodies might be disposed to bring such Reports to the notice of Fellows by inserting the references in one of the issues of their publications.

Appendix.

List of Special Reports presented to Section B during 1898-1902, indicating the type of Special Report to which attention might be drawn in the manner indicated by the Committee:—

1900. "The Constitution of Camphor." By A. Lapworth.
1901. "Methods of Determining the Hydrolytic Dissociation of Salts." By R. C. Farmer.
"On the Equilibrium Law as Applied to Salt Separation and to the Formation of Oceanic Salt Deposits." By E. F. Armstrong.
1902. "Hydro-aromatic Compounds with Single Nucleus." By A. W. Crossley.
"Our Present Knowledge of Aromatic Diazo compounds." By G. T. Morgan.

* Report of the Committee, consisting of Mr. W. A. Shenstone (Chairman), Dr. M. O. Forster (Secretary), Prof. E. Divers, Prof. W. J. Pope, and Dr. A. W. Crossley. Read before the British Association (Section B), Southport Meeting, 1903.

THE CAUSE OF THE LUSTRE PRODUCED ON MERCERISING COTTON UNDER TENSION.*

By JULIUS HÜBNER, F.C.S., and WILLIAM J. POPE, F.R.S.

It is generally supposed that the production of a lustre on treating stretched cotton-yarn with strong caustic soda is conditioned by only two factors—namely, by the simultaneous swelling and shrinking of the fibres. The authors show, however, that a third effect is essential to the production of any appreciable silky lustre; this consists in an uncoiling of the naturally twisted ribbon constituting the cotton-fibre.

On immersing a loose cotton-fibre in strong caustic soda on the microscope stage, it is seen to rapidly untwist, to swell, and at the same time, to shorten in length; the untwisting generally continues until the natural twist has nearly completely disappeared, after which the fibre presents the appearance of a round, irregularly curved rod, with a comparatively smooth surface. If the fibre is fixed at one end and treated with caustic soda, it twists either to the right or to the left, according as it was originally coiled towards the left or towards the right; in the most generally occurring case, that, namely, in which the fibre is coiled partly to the right and partly to the left, the untwisting attending the treatment with soda takes place first towards the left, and then towards the right or *vice versâ*. If the fibre is prevented from contracting by being held at the two ends in a stretched condition it still untwists when treated with soda; since, however, the whole of the untwisting does not take place simultaneously, the untwisting of one part causes another part, which has already become unwound and attained the condition of a gelatinous rod to become tightly twisted in the opposite direction to original twist.

The stretched fibre thus again acquires a corkscrew like appearance, part of the twist being right- and part left handed, with the difference, however, that whilst the raw fibre forms a twisted ribbon creased or folded at the turns treatment with soda converts it into a rod of circular cross-section which has been twisted whilst in a gelatinous state. The twisting of the fibre under these conditions results in the production on the rounded surface of spiral ridges possessing smooth curved contours, which reflect the light at all angles of incidence and reflection just as do the coils of a polished corkscrew. The fibre, therefore, becomes lustrous.

The high degree of transparency possessed by the cotton-fibre introduces difficulties into the microscopic examination of the changes referred to above. But although the fibre is amorphous, it is doubly refracting owing to internal strain; the authors therefore find it convenient to conduct the microscopic examination of the fibre between crossed Nicol prisms, and to accentuate the difference in tint of the

* A Paper read before the British Association (Section B), Southpor Meeting, 1903.

various parts by introducing a one-eighth wave-length retardation plate of mica between the Nicols in such a way that its principal directions make an angle of 45° with those of the prisms. This enables the internal canal, cracks in the surface, and differences in thickness to be made out with great ease. The correctness of the explanation now given of the lustre is shown by a series of photomicrographs taken in natural colours in elliptically polarised light under the conditions just referred to; the authors have to thank their colleague, Mr. Chas. W. Gamble, Director of the Photographic Department in the Manchester Municipal School of Technology, for having assisted the work by the production of these photographs. A further confirmation of the correctness of the conclusions now arrived at is afforded by the observation that whilst cotton-fibres mercerised loose have a practically circular cross-section, fibres treated under tension with soda show cross-sections shaped like polygons with rounded corners.

An independent proof of the authors' conclusions that the untwisting of the fibre is as essential a factor in the production of the gloss as are the swelling and the shrinking, is afforded by an examination of the action of reagents on cotton-yarn. Thus, hanks of a long staple yarn having a mean breaking strength of 417·4±2·1 grms. were immersed loose in caustic soda (sp. gr. 1·342), and saturated barium mercuric iodide solution, and the following changes in the breaking load of the yarn and the lengths of the hanks were found to result:—

Caustic Soda.—Mean breaking load, 526·3±3·8 grms.: shrinkage from 66·0 to 44·8 c.m.

Barium Mercuric Iodide.—Mean breaking load 526·6±3·3 grms.; shrinkage, from 66·0 to 48·9 c.m.

Although the shrinkage and the increase in the breaking load brought about by these two reagents is so nearly the same, yet on immersing hanks under tension in these solutions and washing whilst still under strain, the hank treated with soda acquires a brilliant lustre, whilst that treated with the iodide exhibits only a trace more lustre than the untreated yarn. The explanation of this result is found in the fact that caustic soda causes rapid untwisting of the fibre, whilst barium mercuric iodide does not cause untwisting.

The authors give a list of reagents which bring about two of the three effects shown to be essential to the production of lustre—namely, swelling, shrinking, and untwisting—and find that "lustreing" cannot be effected with such reagents; several solutions are known, however, which cause the three effects, and with the aid of such liquids the lustre can always be produced.

THE APPLICATION OF LOW TEMPERATURES TO THE STUDY OF BIOLOGICAL PROBLEMS.*

By ALLAN MACFADYEN, M.D.

The cellular doctrine lies at the basis of modern biological research. Living matter, in its simple and complex conditions, consists essentially of protoplasm with a contained body, or nucleus. The two elements plasma and nucleus constitute the elementary organism—the cell. The lowest individual forms of life are represented by a single cell, and such unicellular organisms may be either of a vegetable or animal type. The cells in each instance exist as free living and independent organisms. The higher forms of life are built up of parts in which the structural unit remains the cell, despite the modifications the cell necessarily undergoes as a fixed element in the various tissues and organs. All phases of animal and plant life are demonstrably of cellular origin and organisation, and their vital manifestations represent the summed-up activities of cells. Every vital problem, therefore, is ultimately a cellular problem, and a direct study of the cell, in so far as may be possible, is the keynote upon the problem it is desired to investigate. A histological technique aided by the microscope will naturally be employed where it is desired to study the relations of parts and the structural organisation of the tissues and their cellular elements. The soluble products of the living cell spontaneously present themselves for examination by chemical and other means. It is otherwise with regard to the agencies acting and the processes occurring within the confines of the cell. These are naturally beyond the range of the ordinary methods of observation. The essential processes of life are intra-cellular, and intimately bound up with the living substance of the cell, and of these but few data are possessed. The importance of the problems involved is as great as their investigation is difficult. The cell exercises its vital functions in virtue of a specific physical and chemical organisation of its molecular constituents. The ordinary methods of biological and chemical research modify or destroy this organisation, and do not admit of an intimate study of the normal cell constituents. For this purpose, it is essential to eliminate or to reduce to a minimum the influence of external modifying agents on the cell or its immediate products. An intracellular physiology can only be based on a direct study of intra-cellular constituents apart from their secretions and products. This, under ordinary circumstances is impossible with respect to actively functionating and intact cells. It is obvious, therefore, that the first desideratum is a suitable method of obtaining the cell plasma for experimental purposes, and it is only recently that this has been successfully accomplished. The most feasible means of procedure appeared to be the use of *mechanical* agents, which, whilst bringing the cell substance within the field of observation, would at the same time be least likely to affect its character and constitution. The method consists in a mechanical rupture of the cells and the release of their contents under conditions favouring the conservation of their properties. The first successful application of this description of method was made by Buchner in the particular instance of the yeast cell, and with brilliant results. The researches of Buchner were of wide biological significance, and were suggestive of much more than a cell-free alcoholic fermentation of sugars. They demonstrated the possibilities of the new methods with regard to more general vital problems. The Buchner process consisted in a mechanical trituration of the yeast cell with the aid of sand, and a subsequent filtration of the resultant mass under pressure through kieselguhr. The filtrate contained the expressed constituents of the yeast cell which were capable of passing through kieselguhr, and the product, in virtue of its fermentative properties, was termed "Zymase."

The writer and his colleagues have during the past four years been engaged in investigating the application of cognate methods to biological research. The advice and help generously afforded by Professor James Dewar materially forwarded the progress of the research.

It was considered that, by the employment of low temperatures, a disintegration of living cells might possibly be accomplished, and a wide field of inquiry opened to investigation in the biological laboratory. For this purpose the methods of mechanical trituration required refinement in several directions.

The conditions it was desired to fulfil were—a rapid disintegration of the fresh tissues and cells, an avoidance of heat and other modifying agents during the process, and an immediate manifestation of the cellular juices obtained.

It had likewise been noted that ordinary filter pressing through kieselguhr removed physiologically active substances from the cell juices. Liquid air appeared to be the most convenient means of obtaining the necessary cold, and it presented the advantage of a fluid freezing medium, in which the material to be manipulated could be directly immersed. The temperature of this reagent (about −190° C.) would, in addition, prevent heat and chemical changes, whilst reducing the cells to a condition of brittleness favourable to their trituration without the addition of such substances as sand and kieselguhr, which might modify the composition of the resultant product.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

The method, if successful, would meet the conditions desired for the subsequent study of the intra-cellular juices. It may be briefly stated that, by the application of low temperatures, a mechanical trituration of every variety of cell *per se* has been accomplished, and the fresh cell plasma obtained for the purpose of experiment. A number of control experiments have demonstrated that immersion in liquid air is not necessarily injurious to life—bacteria, for example, having survived a continuous exposure for six months to its influence. The actual trituration of the material is accomplished in a specially devised apparatus, which is kept immersed during the operation in liquid air.

The normal and diseased animal tissues have been treated in this manner, and their intra-cellular constituents obtained, *e.g.*, epithelium, cancer tissues, &c.

Moulds, yeasts, and bacteria have been rapidly triturated under the same conditions, and the respective cell juices submitted to examination.

The severest test of the capabilities of the method was furnished by the bacteria—an order of cells for which the standard of measurement is the *mikron*. The experiments proved successful in every instance tested. The typhoid bacillus, for example, is triturated in the short space of two to three hours, and the demonstration has been furnished that the typhoid organism contains within itself a toxin. From these and other researches it has become evident that there exists a distinct class of toxins and ferments which are contained and operate within the cell or bacterium, in contradistinction to the now well-known class of toxins which are extra-cellular, *i.e.*, extruded during life from the cell into the surrounding medium. To this latter class belongs the diphtheria toxin which has been so successfully used in the preparation of diphtheria antitoxin. A number of infective organisms do not produce appreciable extra-cellular toxins, and the search must therefore be made within the specific cells for the missing toxins to which the intoxication of the body in the course of the disease in question is probably due. The practical utility of investigating these intra-cellular toxins has already become evident in the preparation from the intra-cellular toxin of the typhoid bacillus of a cerum having antitoxic value as regards this toxin.

The experiments made with the pus organisms have already shown that intra-cellular toxins exist in this important order of disease germs.

The cell juices of other types of pathogenic bacteria, such as the tubercle and diphtheria bacillus, present characteristics of equal interest.

The application of low temperatures has aided the investigation of certain other biological problems.

The photogenic bacteria preserve their normal luminous properties after exposure to the temperature of liquid air. The effect, however, of a trituration at the same temperature is to abolish the luminosity of the cells in question. This points to the luminosity being essentially a function of the living cell, and dependent for its production on the intact organisation of the cell.

The rabies virus has not yet been detected or isolated, although regarded as an organised entity. The seat of the unknown rabies virus is the nervous system. If the brain substance of a rabid animal be triturated for a given length of time at the temperature of liquid air, its infective properties as regards rabies are abolished. This result appears to be a further indication of the existence in rabies of an organised virus.

The method described admits of a fresh study of the question of immunity from an intra-cellular standpoint.

The intra-cellular juices of the white blood cells have been obtained, and tested with regard to bacteriolytic properties, and the natural protection that may thus be afforded to the body against the invasions of micro-parasites.

The application of low temperatures to the study of biological problems has furnished a new and fruitful method of inquiry.

A STUDY OF MAGNESIUM AND MANGANOUS HYDROXIDES AND OF BARIUM SULPHATE WITH RESPECT TO THE PHENOMENA OF ADHESION AND OF SOLUTION.*

By HARRISON EASTMAN PATTEN.

The work on aluminium,† iron,‡ zinc,§ and chromium‖ has shown that the action of their hydroxides in carrying down other substances into precipitation is chemical, and under certain conditions not proportional to the mass of precipitate. I have examined the action usually expressed by the equation—

$$MgCl_2 + 2KOH = Mg(OH)_2 + 2KCl;$$

also—

$$MgCl_2 + 2KOH + K_2SO_4 = Mg(OH)_2 + 2KCl + K_2SO_4$$

to ascertain whether magnesium hydroxide acts in a similar manner.

Solutions.

Solutions as described below were used in the work :—

1. For the magnesium solution. 20·2963 grms. of crystallised magnesium chloride was made up to 1 litre at 20°. This solution contained 0·0070 grm. chlorine, and 0·00308 grm. magnesium oxide per c.c.

2. A dilute solution of potassium hydroxide standardised by oxalic acid and gravimetrically. It contained 0·0261 grm. potassium hydroxide per c.c.

3. A dilute solution of sulphuric acid, standardised against the potassium hydroxide solution both volumetrically and gravimetrically (weighed as K_2SO_4). It contained 0·04206 grm. sulphuric acid per c.c.

As a preliminary step, the amount of potassium hydroxide required for exact precipitation of the magnesium in solution (1) was determined.

General Method.

The filtrates were analysed and the percentage of each constituent found deducted from that of the total introduced. The difference gives the percentage of the constituent in the precipitate, which may not be analysed directly, since washing or diluting the solution in which the precipitate is formed changes its composition. In the case of magnesium, the precipitated hydroxide is soluble in water.

A blank determination of the magnesium chloride was made :—50 c.c. magnesium chloride stock solution was made up to 500 c.c. at 20°, four portions were drawn off with a 50 c.c. pipette, and the magnesium oxide and chlorine determined in duplicate.

MgO	0·0207 grm.	0·0207 grm.
Cl	0·0040 ,,	0·0042 ,,

Experiments were now made with 44·24 c.c. sulphuric acid, neutralised to potassium sulphate by the equivalent amount of potassium hydroxide, and 50 c.c. stock solution of magnesium chloride as constant factors, the magnesium being precipitated by varying amounts of potassium hydroxide. The above constituents were made up to 500 c.c. at 20°, allowed to stand twenty minutes, well shaken, and four portions of mixed precipitate and solution drawn off with a dry 50 c.c. pipette, and labelled "totals." The solution and precipitate remaining was thrown upon a dry filter-paper, the clear filtrate brought back to 20°, and five portions drawn off with a 50 c.c. pipette, and labelled "filtrates."

The "totals" for magnesium oxide were re-dissolved by

* From the *Journal of the American Chemical Society*, vol. xxv., No. 2.

† "A Thermochemical Analysis of the Reaction between Alum and Potassium Hydroxide," *Am. Chem. Journ.*, viii., 23.

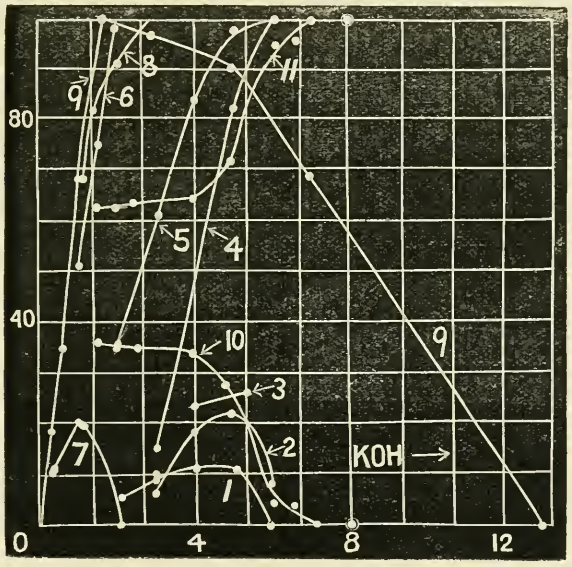
‡ "A Study of Ferric Hydroxide in Precipitation," *Ibid.*, xix., 512.

§ Unpublished.

‖ "Chromic Hydroxide in Precipitation, *Ibid.*, xviii., 608; also "Recherches sur le sulfate chromique, ses transformations et les acides complexes qui en derivent," *Ann. Chem. Phys.*, 1895, vii., 4.

TABLE I.

Experiment.	KOH.	"Total" MgO.		"Filtrate" MgO.		"Precipitate" MgO.	"Total" Cl.		"Filtrate" Cl.		"Precipitate," Cl.	"Precipitate," % MgO.
I.	2	0·02065 0·02071	0·0207	Only a trace.		0·0207	0·0036 0·0035	0·0036	0·0037 0·0040	0·0038	0·0000	100·00
II.	6 (2) 300 c.c. $MgCl_2$	0·1190+ 0·1190 −	0·1190	0·0026 0·0020	0·0023	0·1167	0·2082 0·2085	0·2084	0·2086 0·2088	0·2087	0·0000	98·06
III.	6 ($1\frac{1}{2}$) 300 c.c. $MgCl_2$	0·1174 0·1180	0·1177	0·0281 0·0276	0·0278	0·0899	0·2080 0·2085	0·2083	0·2081 0·2087	0·2084	0·0000	76·38
New Solution.												
IV.	$1\frac{1}{2}+K_2SO_4$	0·1926 0·1927	0·1926	0·0480 0·04807	0·0480	0·1446	0·3445 0·3443	0·3444	0·3442 0·3438	0·3440	0·0004	75·07
V.	$1\frac{1}{2}$	0·1928 0·1931	0·1929	0·0484 0·0481	0·0482	0·1447	0·3431 0·3432	0·3431	0·3427 0·3429	0·3428	0·0003	75·07
VI.	$1+K_2SO_4$	0·1936 0·1942	0·1939	0·0958 0·0963	0·0960	0·0979	0·3430 0·3425	0·3427	0·3433 0·3429	0·3431	0·0000	50·46
VII.	1	0·1941 0·1940	0·1940	0·0968 0·0966	0·0966	0·0974	0·3426 0·3429	0·3427	0·3427 0·3426	0·3426	0·0001	50·46



hydrochloric acid in some excess, ammonia added to alkaline reaction, and the magnesium precipitated cold as magnesium ammonium phosphate, and weighed as pyrophosphate.

The "totals" for chlorine were re-dissolved by nitric acid, precipitated hot with silver nitrate solution, and the magnesium removed by a wash-water containing 25 c.c. concentrated nitric acid and 0·1 grm. silver nitrate per litre. The chlorine was then weighed as silver chloride.

The "filtrates" for magnesium oxide and chlorine were analysed in the same manner as the "totals." As in the work with aluminium, chromium, iron, and zinc, it was assumed that resolution by hydrochloric or nitric acid would liberate any constituents carried down in the precipitation with potassium hydroxide.

It was considered unnecessary to determine the potassium oxide in the "totals" and "filtrates," for two reasons:—First, because in all the foregoing work in this line no carrying down of potassium was observed short of resolution in the alkali; second, the negative results of the work on magnesium oxide, chlorine, and sulphur trioxide in this investigation indicate the absence of such action.

No good method of separating the magnesium oxide from the sulphur trioxide in "totals" and "filtrates" being available, two different methods were used to ascertain whether the sulphur trioxide enters into the reaction.

1. The amount of magnesium oxide precipitated in presence of *potassium sulphate* by a definite amount of potassium hydroxide, should be greater than the amount precipitated in absence of the sulphate—*if sulphur trioxide enters into the reaction.**

2. Magnesium oxide or chloride should be carried down into precipitation by barium sulphate. The four elements already mentioned show this reciprocal action, as does also manganese, of which I shall speak later.

Experiment I.—The system was made up according to the equation $MgCl_2+2KOH=Mg(OH)_2+2KCl$, using 50 c.c. of magnesium chloride solution to 22·2 c.c. potassium hydroxide solution. No potassium sulphate was introduced here, since the object was to determine if chlorine were carried down into precipitation by the magnesium hydroxide. No chlorine was found in the precipitate (see Table I., Exp. I.). A trace of magnesium was obtained in the filtrate by further addition of potassium hydroxide, showing that magnesium chloride is not completely precipitated by 2 molecules of potassium hydroxide. As the mass of precipitate was so small, for this concentration, and as "adhesion" in the cases of chromium, iron, aluminium, and zinc hydroxides is more marked in concentrated solutions,

* Series II., "Chromic Hydroxide in Precipitation," *loc. cit.*, "A Study of Ferric Hydroxide in Precipitation" *loc. cit.*

the next two experiments were made up each with six 50 c.c. portions of magnesium chloride solution instead of one 50 c.c. portion as in this experiment.

Experiment II.—The system was made up according to the equation $MgCl_2+2KOH = Mg(OH)_2+2KCl$ (see Table I., Exp. II., for results). This shows no chlorine carried down into precipitation. Since adhesion is more marked at incomplete precipitation than at complete precipitation, in the next experiment I used 1½KOH.

Experiment III.—The system was made up according to the equation $MgCl_2+1\frac{1}{2}KOH = ?$ (see Table I., Exp. III., for results). Here again no chlorine is carried down by the precipitate.

The stock supply of magnesium chloride being now exhausted, a new solution (4) was made up:—203 grms. $MgCl_2+6H_2O$ were dissolved in water, and diluted to 1000 c.c. of solution at 20° C. One 50 c.c. portion was drawn off, and made up to 500 c.c. at 20° C. Of this solution each 50 c.c. contained:—

MgO	0·1926 grm.	0·1925 grm.
Cl..	0·3445 „	0·3440 „

For 50 c.c. of stock solution of magnesium chloride (4), 212·5 c.c. potassium hydroxide were required to precipitate completely the magnesium. The calculated amount of potassium hydroxide was 207 c.c.

Now the attempt was made to ascertain if sulphur trioxide is carried down into precipitation. As was stated in "General Method," no good means of separation being at hand, a difference method was resorted to. The work on chromium and iron showed that in a partially precipitated system (which had been filtered or allowed to settle) further precipitation was caused by the addition of a little sulphate solution, and in some cases* no definite precipitate was obtained unless some soluble sulphate was present. From this influence of sulphur trioxide on the amount of hydroxide formed at fractional precipitation, I assume that if sulphur trioxide is carried down into precipitation by magnesium hydroxide, the amount of magnesium hydroxide precipitated by, say, 1·5 molecules of potassium hydroxide will be greater in the presence of sulphur trioxide than in its absence. If then, the amount of magnesium hydroxide precipitated by 1·5 molecules of potassium hydroxide is the same with and without sulphur trioxide present, I conclude that no adhesion takes place.

For results see Experiments IV., V., VI., VII., Table I., and the accompanying plate, curve 6.

The same amount of magnesia is precipitated in Experiment IV. with potassium sulphate present as in Experiment V. with potassium sulphate absent; likewise in Experiments VI. and VII. Since no sulphur trioxide is carried down into precipitation at these fractional points it was considered unnecessary to try an experiment at complete precipitation, inasmuch as the other elements worked with show their greatest "adhesion" activity at these points. Further, since magnesium gives a definite precipitate at the fractional points in absence of sulphur trioxide, it ought to carry down chlorine into precipitation if it exercises the property of "adhesion"; Experiments I., II., and III., show no chlorine carried down.

Experiment VIII.—It was determined that magnesium hydroxide precipitated from magnesium chloride by potassium hydroxide in aqueous solution does not re-dissolve in excess of potassium hydroxide.

Experiment IX.—Twelve different barium sulphate determinations which had been made from solutions containing magnesium chloride, potassium, sulphate, and hydrochloric acid by addition of barium chloride were treated as follows:—Fused with sodium carbonate, the alkali washed out with water, the insoluble barium carbonate dissolved in hydrochloric acid, re-precipitated by ammonium carbonate to remove the barium, and the filtrate tested for magnesium by sodium hydrogen phosphate. Not a trace of magnesium was found.

Discussion.

These results may be summarised thus:—(1) Magnesium hydroxide does not carry down into precipitation with it either chlorine or sulphur trioxide. (2) Barium sulphate does not carry down into precipitation either magnesium oxide or chloride. (3) More than the theoretical amount of potassium hydroxide is required to completely precipitate magnesium hydroxide from a magnesium chloride solution in water at the concentration and temperature studied. On this last point more work should be done.

(To be continued).

* Fractional precipitation of chromium chloride by less than three molecules of potassium hydroxide. See "Chromic Hydroxide in Precipitation," *loc cit.*

FREEZING-POINT CURVES FOR BINARY SYSTEMS.*

By JAMES C. PHILIP, M.A., B.Sc., Ph.D.

When a liquid mixture of two components is slowly cooled, separation of solid will take place at some temperature. For complete interpretation of the phenomena, it is necessary to know not only (1) this temperature of initial freezing, but also (2) the composition of the separating solid, and (3) the composition of the liquid with which this solid is in equilibrium. The varying character of the relationship between (2) and (3) is best seen by plotting the one against the other in a square diagram. It is found then that the experimentally known cases fall into one or other of two classes, according as the composition of the separating solid varies continuously with that of the liquid from which it separates, or is for certain ranges of concentration definite and constant. To the former class belong systems of components that form mixed crystals; to the latter class belong systems of components that, forming no mixed crystals, may form definite compounds.

If now attention is confined to the latter class, and the freezing-point curves (that is, the curves showing the relationship between the temperature of initial freezing and the composition of the liquid) are considered for such systems, experimental work shows that to each range of concentration over which the composition of the separating solid is definite and constant, there corresponds a branch of the freezing-point curve. There are always at least two such branches over which separation of the pure components takes place, and there may be one or more intermediate branches with a maximum or summit over which separation of definite compounds takes place (see, for example, Guthrie, *Phil. Mag.*, 1884, xvii., 643; Dahms, *Wied. Ann.*, 1895, liv., 486; Stortenbeker, *Zeit. Physikal. Chem.*, x., 194; Heycock and Neville, *Phil. Trans.*, A., cxciv., 201; Kuriloff, *Zeit. Physikal. Chem.*, 1897, xxiii., 547, 673; Philip, *Journ. Chem. Soc.*, 1903, lxxxiii., 814). The composition at a summit-point on a freezing-point curve is exactly that of the corresponding straight line on the square diagram referred to above, and thus the occurrence of an intermediate mound on the freezing-point curve is to be taken as evidence that the components form a compound, the composition of which is given by the summit-point. It is further to be observed that the various branches of a freezing-point curve cut each other at an angle, as shown by the fact that a branch can be continuously realised beyond its point of section with another branch; illustrations of this are found in Roozeboom's work on the hydrates of ferric chloride and in the author's study (*loc. cit.*) of the freezing-point curve for mixtures of phenol and α-naphthylamine.

Beyond these general characteristics of freezing-point curves, there are certain special features that are of interest, and that have received illustration in some recent work. For example, there may be an intermediate branch that

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

does not reach a summit, pointing to the formation of a compound that is unstable at its own melting-point. A case in point is supplied by Donnan and Burt's work on the hydrates of lithium nitrate (*Journ. Chem. Soc.*, 1903, lxxxiii., 335), and to a certain extent by the author's work on the freezing-point curve for phenol and urea. These two form a compound containing one molecule of urea to two of phenol, and the freezing-point curve shows a corresponding branch that just reaches a summit, where it is cut by another branch along which separation of urea takes place. The passage from one branch to another, as in this case of phenol and urea, is marked by an obvious change in the character of the primary crystallisation, and by the existence of secondary or eutectic freezing-points on the same level as the intersection of the two branches.

The freezing-point curve becomes especially interesting when the two components form a dimorphous compound. While the general rule still holds that for each solid form there is a branch of the freezing-point curve, the one branch in this case is found to envelope the other, the two summit-points occurring at the same composition. The only cases where this bearing of dimorphism on the freezing-point curve has been studied are Stortenbeker's investigation (*loc. cit.*) of the freezing-point curve of iodine and chlorine, and the author's work (*loc. cit.*) on that of phenol and *p*-toluidine. In this latter case a compound is formed which exists in two modifications (as plates and needles), and when a liquid mixture containing from 30—60 molecular per cent of *p*-toluidine is allowed to cool, a primary crystallisation of plates is observed, the freezing-point being obtained in the usual manner. Presently a transformation of the plates into the more stable needles takes place; this is accompanied by a rise of temperature, and a second freezing-point is obtained, generally about 1·5° higher than the one first observed. These observations may be repeated with mixtures of different composition, and thus two branches of the freezing-point curve are obtained, the one of which, as has been said, envelopes the other.

THE INFLUENCE OF SMALL QUANTITIES OF WATER IN BRINGING ABOUT CHEMICAL REACTION BETWEEN SALTS.*

By EDGAR PHILIP PERMAN, D.Sc.

Many experimenters have investigated the influence of traces of moisture in reactions between gases, but so far as I am aware no one has hitherto made similar experiments with solids.

The substances chosen for experiment were salts of lead or mercury, and salts of potassium, usually the iodide, which would show the occurrence and progress of a reaction by a colour change.

a. Experiments with Lead Chloride and Potassium Iodide.—Equivalent quantities of the two salts were dried over strong sulphuric acid in a suitable apparatus, and then mixed; it was found that after forty-eight hours' drying no visible change took place on mixing the salts, but on keeping the mixture for a week (in a sealed flask) a faint yellow colour appeared, which gradually deepened, until after some months it became a bright yellow.

Attempts were made to discover how much water was necessary in order to make the reaction immediately visible; the results were not very concordant, but indicated about 0·5 m.grm. as the amount necessary in the conditions of the experiment, viz. 2 grms. of potassium iodide and an equivalent quantity of lead chloride were mixed in a glass flask of about 100 c.c. capacity.

b. Experiments with other Lead Salts and Potassium Iodide.—Lead formate and lead nitrate were found to act in a similar way to the chloride.

Lead sulphate reacts much more slowly, although exposed to the air, while the carbonate and the oxide react very slowly indeed.

c. Experiments with Mercuric Chloride and Potassium Iodide.—Mercuric chloride and potassium iodide treated in exactly the same way as already described gave a strong red colouration on mixing; the same result was obtained when commercial phosphoric anhydride was used as a drying agent. By drying with specially prepared phosphoric anhydride, however, the mixture obtained has been kept for some months without change.

d. Other Experiments with Mercuric Salts.—Mercuric cyanide showed no reaction with potassium iodide.

Mercuric chloride and potassium chromate reacted very slowly, although exposed to the air.

Discussion of Results.—There is no reason for thinking that these reactions take place in any way essentially different from similar reactions in solution, and I believe that the only difference is the extreme slowness of the reaction. It is noteworthy that the velocity of the reaction between mercuric chloride and potassium iodide is enormously greater than that between lead chloride and potassium iodide when dried in the same way. The factors to which this difference may be referred are (1) solubility, (2) volatility, (3) degree of ionisation, (4) specific reaction velocity. We will consider these in order.

1. Mercuric chloride is about ten times as soluble as lead chloride in cold water, but this alone would not account for the difference; *e.g.*, mercuric cyanide is still more soluble, but does not react at all.

2. Judging from the boiling-points, mercuric chloride would appear to be more volatile than lead chloride, the boiling-point of the former being 300° C., and that of the latter about 900° C.; but I find that on aspirating air over each salt, and then over potassium iodide, the vapour from the lead chloride affects the potassium iodide much the sooner.

The difference in the speed of the two reactions (*a* and *c*) cannot therefore be caused by the difference in volatility.

3. The degree of ionisation cannot be the cause of the difference noted, for mercuric chloride is known to be very slightly ionised in solution, while lead chloride may be taken as completely ionised.

4. The specific reaction velocity appears to be the real determining factor, and the reaction is probably of the form $AB + CD = AD + BC$. If it is only free ions that react (which seems to me improbable), then the velocity of ionisation in the case of mercuric chloride must be extremely great.

There may also be other factors at present unknown.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

CORRESPONDENCE.

COSMICAL RADIO-ACTIVITY.

To the Editor of the Chemical News.

Sir,—In a paper entitled "Cosmical Radio-activity" read before the British Association, and reprinted in the Chemical News (vol. lxxxviii., p. 166), Mr. Arthur Schuster suggests that radio-activity may be a common property of all matter—the apparently inactive metals possessing it in so small a degree that our power of observation is insufficient to detect it. May I be allowed to point out that this view is not new, but has already been put forward and discussed by me in your columns more than two-and-a-half years ago; *vide* Chemical News, March 15, 1901 (vol. lxxxiii.; p. 130), and again on May 2, 1902 (vol. lxxxv., p. 205)? Since that time, of course, an enormous extension of our knowledge has been made concerning radio-activity, but I see no cause to alter the views then put forward, except that, in the last paper referred to above, I have probably exaggerated the effect of temperature.—I am, &c.,

Geoffrey Martin.

Kiel, October 5, 1903.

NOTICES OF BOOKS.

Foods: Their Composition and Analysis. By Alexander Wynter Blyth, M.R.C.S., F.I.C., F.C.S., &c., and Meredith Wynter Blyth, B.A. (Cantab), B.Sc. (Lond.), F.I.C., F.C.S., &c. Fifth Edition. London: Charles Griffin and Co., Ltd. 1903.

The fifth edition of this standard work on Food Analysis has been to a great extent re-written, some portions having been greatly enlarged, while others have been condensed or omitted. Chapters on the detection and determination of arsenic and the bacteriology of water, &c., have been added, and in every respect the text has been brought up to date; the account of the present state of the law in England with regard to the adulteration of food, and the text of Adulteration Acts. will be found very useful by public analysts. The position of this work is thoroughly established, and it is well known and properly regarded as almost indispensable by all engaged in analytical chemistry, so that it is unnecessary to do more than indicate the special features of this latest edition, which contains much fresh useful matter.

Ausgewählte Methoden der Analytischen Chemie. Zweiter Band. ("Select Methods of Analytical Chemistry." Volume II.). By Prof. Dr. A. Classen. Braunschweig: Friedrich Vieweg und Sohn. 1903.

The second volume of this book contains an account of the application of the methods of analytical chemistry to the non-metallic elements and their compounds. The most modern and accurate methods of analysis, both qualitative and quantitative, are given with sufficient explicitness and detail for the student to carry out all the operations described without further assistance. Special applications of the various processes are mentioned, and technical methods are also discussed. The analysis of water is particularly fully described, and the chapters on the treatment of explosives may also be mentioned as excellent; the elementary analysis of organic compounds is included among the subjects dealt with. This work is undoubtedly one of the most complete of its class extant, and can be thoroughly recommended.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 11, September 14, 1903.

Simplicity of the Spectra of Cathode Light in Gases containing Nitrogen and Carbon.—H. Deslandres.—In the simple gases containing nitrogen and carbon, cathode light is remarkably simple, and this property can be further studied by examining the intimate nature of the phenomenon. In 1890 the author investigated the reasons upon which the structure and chemical formula of illuminating gases depend, also the number and the grouping of the rays whose repetition gives rise to the spectrum bands. The numerous spectra of carbon and nitrogen which are examined are due to the different allotropic states of the simple bodies or their compounds with the elements of water. Under these conditions the spectra of the positive pole formed by the repetition of multiple rays correspond to molecules containing several atoms; the negative spectra, on the contrary, are due to a single atom. It may also be stated that the cathode light, which, when feeble, ionises gases, when stronger will also illuminate them, giving band spectra, and, by so doing, decomposes them into their simplest chemical elements. When the electric spark becomes more powerful the bands disappear, giving place to lines.

Action of a Trace of Water on the Decomposition of Alkaline Hydrides by Acetylene.—Henri Moissan.—The author's present series of experiments investigate the action of a trace of water on a chemical reaction. They correspond to those experiments which he has already described *à propos* of the synthesis of formates by means of carbon dioxide and the hydrides. Dry acetylene gas does not act on potassium hydride, except at temperatures above $+42^{0}$. If the gas, however, contains a trace of water, this latter modifies the conditions of the reaction, so that it takes place at ordinary temperatures. The author attributes this change to the evolution of heat, which, once started at a particular point, causes an elevation of temperature which raises the hydride to $+42^{0}$, and so causes the reaction to take place.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Separation of Methyl from Ethyl Alcohol.—I should be very much obliged if some reader would supply a description of a method or methods (not necessarily commercial) by which methyl may be separated from ethyl alcohol in a simple mixture of the two alcohols, with a view of recovering the latter alcohol; and also a method of detecting the presence of methyl alcohol in the presence of its next higher homologue.—S. J. Hill, New South Wales.

MEETINGS FOR THE WEEK.

Wednesday, 21st.—Microscopical, 8. "Report on the Recent Foraminifera of the Malay Archipelago" (Part XV.), by Fortescue W. Millett, F.R.M.S. Exhibition of Drawings and Slides of British Hydrachnidæ, by C. D. Soar, F.R.M.S.

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RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 198).

Chapter III. (*continued*).[1]

Polonium is particularly well adapted to the study of α-rays, because the specimens which we possess emit no other kind of rays. I made a preliminary series of experiments with extremely active recently prepared specimens of polonium. I found the absorbability of the rays to increase with increase of thickness of the matter traversed. This singular law of absorption is contrary to that known for other kinds of radiation.

I employed for this research our apparatus for the determination of electrical conductivity arranged in the following manner :—

The two plates of a condenser, P P and P' P' (Fig. 8), are horizontally disposed in a metallic box, B B B B, connected to earth. The active body, A, placed in a thick metallic box, C C C C, connected with the plate P' P', acts upon the air of the condenser across a metallic sheet, T ; the rays which pass through the sheet are alone utilised for producing the current, the electric field being limited by the sheet. The distance, A T, of the active body from the sheet may be varied. The field between the plates is established by means of a battery. By placing in A upon the active body different screens, and by adjusting the distance A T, the absorption of rays which travel long or short distances in the air may be determined.

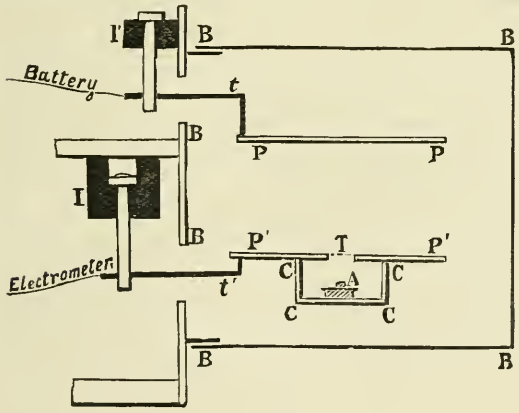


Fig 8.

The following are the results obtained with polonium :—

For a certain value of the distance A T (4 c.m. and more), no current passes ; the rays do not penetrate the condenser. When the distance A T is diminished, the appearance of the rays in the condenser is manifested somewhat suddenly, a weak current changing to one of considerable strength for a slight diminution of distance ; the current then increases regularly as the active body continues to approach the sheet T.

When the active body is covered with a sheet of aluminium $\frac{1}{10}$ m.m. thick, the absorption produced by the lamina becomes greater, the greater the distance A T.

If a second similar lamina of aluminium be placed upon the first, each absorbs a fraction of the radiation it receives, and this fraction is greater for the second lamina than for the first.

In the following table I have represented in the first line the distances in centimetres between the polonium and the sheet T ; in the second line the percentage of the rays transmitted by a sheet of aluminium ; in the third line the percentage of the rays transmitted by two sheets of the same aluminium :—

Distance A T	3·5	2·5	1·9	1·45	0·5
Percentage of rays transmitted by one lamina	0	0	5	10	25
Percentage of rays transmitted by two laminæ	0	0	0	0	0·7

In these experiments the distance of the plates, P and P', was 3 c.m. We see that the interposition of the aluminium screen diminishes the intensity of the radiation to a greater degree at further distances than at nearer distances.

This effect is still more marked than the preceding figures seem to indicate. For a distance of 0·5 c.m. 25 per cent represents the mean penetration for all the rays which pass beyond this distance. If, for example, only those rays between 0·5 c.m. and 1 c.m. be comprehended, the penetration would be greater. And if the plate P be placed at a distance of 0·5 c.m. from P' the fraction of the radiation transmitted by the aluminium lamina (for A T = 0·5 c.m.) is 47 per cent, and through two laminæ it is 5 per cent of the original radiation.

I have recently performed a second series of experiments with these same specimens of polonium, the activity of which was considerably diminished, the interval of time between the two series of experiments being three years.

In the former experiments, polonium nitrite was used ; in the latter, the polonium was in the state of metallic particles obtained by fusing the nitrite with potassium cyanide.

I found that the radiation of polonium had preserved its essential characteristics, and I discovered new results. The following, for different values of the distance A T, are the fractions of the radiation transmitted by a screen composed of four superposed very thin leaves of beaten aluminium.

Distance A T, in centimetres	0	1·5	2·6
Percentage of rays transmitted by the screen	76	66	39

I also found that the fraction of the radiation absorbed by a given screen increases with the thickness of the material already traversed by the radiation, but this only occurs after the distance A T has reached a certain value. When this distance is zero (the polonium being in contact with the sheet, either outside or inside the condenser), it is observed that with several similar superposed screens, each absorbs the same fraction of the radiation it receives ; otherwise expressed, the intensity of the radiation diminishes therefore according to an exponential law as a function of the thickness of the material traversed, as in the case of homogeneous radiation transmitted by the lamina without changing its nature.

The following numerical results are given with reference to these experiments :—

For a distance A T equal to 1·5 c.m. a thin aluminium screen transmits the fraction 0·51 of the radiation it receives when acting alone, and the fraction 0·34 of the radiation it receives when it is preceded by another similar screen.

On the contrary, for a distance A T equal to zero, the same screen transmits in both the cases considered the same fraction of the radiation it receives, and this fraction is equal to 0·71 ; it is therefore greater than in the preceding case.

The following numbers indicate for a distance A T equal to 0 and for a succession of thin superposed screens, the ratio of the radiation transmitted to the radiation received for each screen :—

* Thesis presented to the Faculté des Sciences de Paris.

Series of nine very thin copper leaves.	Series of seven very thin aluminium leaves.
0·72	0·69
0·78	0·94
0·75	0·95
0·77	0·91
0·70	0·92
0·77	0·93
0·69	0·91
0·79	
0·68	

Taking into account the difficulties of the manipulation of very thin screens and of the superposition of screens in contact, the numbers of each column may be looked upon as constant; the first number only of the aluminium column indicates a greater absorption than that indicated by the following numbers.

The α-rays of radium behave similarly to the rays of polonium. These rays may be investigated almost isolated by deflecting to one side the β-rays with the magnetic field; the γ-rays seem of slight importance in comparison with the α-rays. The operation can only be carried on at some distance from the source of radiation. The following are the results of an experiment of this kind. The fraction of the radiation transmitted by a lamina of aluminium 0·01 m.m. thick is measured; this screen was placed always in the same position, above and at a little distance from the source of radiation. With the apparatus of Fig. 5, the current produced in the condenser for different values of the distance A D is observed, both with and without the screen:—

Distance A D	6·0	5·1	3·4
Percentage of rays transmitted by the aluminium	3	7	24

The rays which travel furthest in the air are those most absorbed by the aluminium. There is therefore a great similarity between the absorbable α-rays of radium and the rays of polonium.

The deflected β-rays and the undeflected penetrating γ-rays are, on the contrary, of a different nature. The experiments, notably of MM. Meyer and von Schweidler, clearly show that, considering the radiation of radium as a whole, the penetrating power of this radiation increases with the thickness of the material traversed, as is the case of Röntgen rays. In these experiments the α-rays produce scarcely any effect, being for the most part suppressed by very thin absorbent screens. Those which penetrate are, on the one hand, β-rays more or less scattered; on the other hand, γ-rays, which appear similar to Röntgen rays.

The following are the results of some of my experiments on the subject:—

The radium is enclosed in a glass vessel. The rays, which emerge from the vessel, traverse 30 c.m. of air, and are received upon a series of glass plates, each of thickness 1·3 m.m.; the first plate transmits 49 per cent of the radiation it receives, the second transmits 84 per cent of the radiation it receives, the third transmits 85 per cent of the radiation it receives.

In another series of experiments the radium was enclosed in a glass vessel placed 10 c.m. from the condenser which received the rays. A series of similar screens of lead each 0·115 m.m. thick were placed on the vessel.

The ratio of the radiation transmitted to the radiation received is given for each of the successive screens by the following numbers:—

0·40 0·60 0·72 0·79 0·89 0·92 0·94 0·94 0·97

For a series of four screens of lead, each of which was 1·5 m.m. thick, the ratio of the radiation transmitted to the radiation received was given for the successive screens by the following numbers:—

0·09 0·78 0·84 0·82

The results of these experiments shows that when the thickness of the lead traversed increases from 0·1 m.m. to 6 m.m., the penetrating power of the radiation increases.

I found that, under the experimental conditions mentioned, a screen of lead 1·8 c.m. thick transmits 2 per cent of the radiation it receives; a screen of lead 5·3 c.m. thick transmits 0·4 per cent of the radiation it receives. I also found that the radiation transmitted by a thickness of lead of 1·5 m.m. consists largely of rays capable of deflection (cathode order). The latter are therefore capable of traversing not only great distances in the air, but also considerable thicknesses of very absorbent solids, such as lead.

In investigating with the apparatus of Fig. 2 the absorption exercised by an aluminium screen 0·01 m.m. thick upon the total radiation of radium, the screen being always placed at the same distance from the radiating body, and the condenser being placed at a variable distance, A D, the results obtained are the sum of those due to the three groups of the radiation. At a long distance the penetrating rays predominate, and the absorption is slight; at a short distance the α-rays predominate, and the absorption becomes less with nearer approach to the substance; for an intermediate distance the absorption passes through a maximum and the penetration through a minimum.

Distance A D	7·1	6·5	6·0	5·1	3·4
Percentage of rays transmitted by aluminium ..	91	82	58	41	48

Certain experiments made in connection with absorption always demonstrate a certain similarity between the α-rays and the β-rays. Thus it was that M. Becquerel discovered that the absorbent action of a solid screen upon the β-rays increases with the distance of the screen from the source, such that if the rays are subjected to a magnetic field, as in Fig. 4, a screen placed in contact with the source of radiation allows a larger portion of the magnetic spectrum to be in evidence than does the same screen placed upon the photographic plate. This variation of the absorbent effect of the screen with the distance of the screen from the source is similar to that which occurs with the α-rays; this has been verified by MM. Meyer and von Schweidler, who operated by means of the fluoroscopic method; M. Curie and I observed the same fact when working by the electrical method. However, when the radium is enclosed in a glass tube and placed at a distance from the condenser, which is itself enclosed in a thin aluminium box, it becomes a matter of indifference whether the screen be placed against the source or against the condenser; the current obtained is the same in both cases.

The investigation of the α-rays led me to the reflection that these rays behave like projectiles having a certain initial velocity, and which lose their force on encountering obstacles. These rays, moreover, travel by rectilinear propagation, as has been shown by M. Becquerel in the following experiment:—Polonium emitting rays was placed in a very narrow straight cavity hollowed in a sheet of cardboard. Thus a linear source of radiation was produced. A copper wire, 1·5 m.m. in diameter, was placed parallel and opposite to the source at a distance of 4·9 m.m. Beyond was placed a parallel photographic plate at a distance of 8·65 m.m. After an exposure of ten minutes, the geometric shadow of the wire was perfectly reproduced, with a narrow penumbra corresponding to the size of the source. The same experiment succeeded equally well when a double leaf of beaten aluminium was placed against the wire, through which the rays must pass.

There are therefore rays capable of giving perfect geometric shadows. The experiment with the aluminium shows that these rays are not scattered in traversing the screen, and that this screen does not give rise to any noticeable extent to secondary rays similar to the secondary rays of the Röntgen rays.

The experiments of Mr. Rutherford show that the projectiles which constitute the α-rays are deflected by a magnetic field, as if they were positively charged. The deflection in a magnetic field becomes less as the product $\frac{m v}{e}$ becomes greater; m being the mass of the particle, v its velocity, and e its charge. The cathode rays of radium

are but slightly deflected, because their velocity is enormous; they are, on the other hand, very penetrating, because each particle has a very small mass together with a great velocity. But particles which, with an equal charge and a less velocity, have a greater mass, would be also only slightly influenced by the action of the field, and would give rise to very absorbable rays. From the results of Mr. Rutherford's experiments, this seems to take place in the case of the α-rays.

The penetrating γ-rays appear to be of quite another nature, and similar to Röntgen rays.

We have now seen how complex a phenomenon is the radiation of radio-active bodies. The difficulties of investigation are increased by the question as to whether the radiation undergoes a merely selective absorption on the part of the material, or whether a more or less radical transformation.

Little is so far known with regard to this question. If the radiation of radium be regarded as containing rays both of the cathode and Röntgen species, it might be expected to undergo transformations in traversing screens. It is known:—Firstly, that cathode rays emerging from a Crookes tube through an aluminium window are greatly scattered by the aluminium; and, further, that the passage through the screen entails a diminution of the velocity of the rays. In this way, cathode rays with a velocity equal to $1{\cdot}4 \times 10^{10}$ c.m. lose 10 per cent of their velocity in passing through 0·01 m.m. of aluminium. Secondly, cathode rays on striking an obstacle give rise to the production of Röntgen rays. Thirdly, Röntgen rays, on striking a solid obstacle, give rise to the production of *secondary rays*, which partly consist of cathode rays.

The existence, by analogy, of all these preceding phenomena may therefore be predicted for the rays of radio-active substances.

In investigating the transmission of polonium rays through a screen of aluminium, M. Becquerel observed neither the production of secondary rays nor any transformation into cathode rays.

I endeavoured to demonstrate a transformation of the rays of polonium by using the method of interchangeable screens. Two superposed screens, E_1 and E_2, being traversed by the rays, the order in which they are traversed should be immaterial if the passage through the screens does not transform the rays; if, on the contrary, each screen transforms the rays during transmission, the order of the screens is of moment. If, for example, the rays are transformed into more absorbable rays in passing through lead, and no such effect is produced by aluminium, then the system lead-aluminium will be more opaque than the system aluminium-lead; this takes place with Röntgen rays.

My experiments show that this phenomenon is produced with the rays of polonium. The apparatus employed was that of Fig. 8. The polonium was placed in the box, c c c c, and the absorbing screens, of necessity very thin, were placed upon the metallic sheet, T.

Screens employed.	Thickness. M.m.	Current observed.
Aluminium Brass	0·01 0·005	17·9
Brass Aluminium	0·005 0·01	6·7
Aluminium Tin	0·01 0·005	150
Tin Aluminium	0·005 0·01	125
Tin Brass	0·005 0·005	13·9
Brass Tin	0·005 0·005	4·4

The results obtained prove that the radiation is modified in passing through a solid screen. This conclusion accords with the experiments in which, of two similar superposed metallic screens, the first is less absorbent than the second. From this it is probable that the transforming action of a screen increases with the distance of the screen from the source. This fact has not been verified, and the nature of the transformation has not been studied in detail.

I repeated the same experiments with a very active salt of radium; the result was negative. I only observed insignificant variations in the intensity of the radiation transmitted with interchange of the order of the screens. The following systems of screens were experimented with:—

Aluminium, thickness	.. ..	0·55	m.m.
,,	,, ...	0·55	,,
,,	,, ...	0·55	,,
,,	,, ...	1·07	,,
,,	,, ...	0·55	,,
,,	,, ...	1·07	,,
,,	,, ...	0·15	,,
,,	,, ...	0·15	,,
,,	,, ...	0·15	,,
Platinum,	,, ...	0·01	,,
Lead,	,, ...	0·1	,,
Tin,	,, ...	0·005	,,
Copper,	,, ...	0·05	,,
Brass,	,, ...	0·005	,,
,,	,, ...	0·005	,,
Platinum,	,, ...	0·01	,,
Zinc,	,, ...	0·05	,,
Lead,	,, ...	0·1	,,

The system lead-aluminium was slightly more opaque than the system aluminium-lead, but the difference was not great.

Thus, I was unable to discover an appreciable transformation of the rays of radium. However, in various radiographic experiments, M. Becquerel observed very intense effects due to scattered or secondary rays, emitted by solid screens which received radium rays. Lead seemed to be the most active substance in this respect.

(To be continued).

Action of the Hydrated Oxide of Cadmium on the Ammoniacal Salts.—H. Grossmann.—While examining the action of the hydrated oxide of cadmium on solutions of the ammoniacal salts, the author obtained results different to those announced by Tassilly (*Ann. Chim. Phys.*, [7], vol. xvii., p. 107). By the prolonged boiling of a solution of sal-ammoniac with an excess of oxide of cadmium, a liquor was obtained which deposits first of all a mixture of the ammoniacal chloride, $CdCl_2(NH_3)_2$, and the double chloride, then a mixture of rhombohedra, ($CdCl_2$,$4NH_4Cl$), and of needles, ($CdCl_2$,NH_4Cl), and, finally, large crystals of the double chloride containing $4NH_4Cl$. These latter crystals are decomposed by water, as announced by Rünbach (*Berichte*, vol. xxx., p. 3073), giving 3 molecules of NH_4Cl, and the chloride $CdCl_2$,NH_4Cl. With bromide of cadmium, under the same conditions as above, the author obtained the ammoniacal bromide, $CdBr_2$,$(NH_3)_2$, and then bromide of ammonium. By leaving the solution over sulphuric acid, monoclinic crystals of $CdBr_2$,$4NH_4Br$ can be obtained; these are decomposed by water like the corresponding chlorised compounds. The mother-liquors still contain the monobromide, $CdBr_2$,NH_4Br,$\frac{1}{2}H_2O$, which is not decomposed by water. This salt, which is always contaminated with the salt containing $4NH_4Br$, is, however, easily prepared from its constituents. The action of cadmium hydrate on iodide of ammonium in the same manner gives the compounds, CdI_2,$(NH_3)_2$ and CdI_2,NH_4I,H_2O.—*Zeit. Anorg. Ch.*, vol. xxxiii., p. 49.

THE ULTRA-VIOLET SPECTRUM OF RADIUM.*

By Sir WILLIAM CROOKES, F.R.S.

The spectrum of radium has been examined and the wave-lengths of many of its lines given by several observers, amongst whom I may include Exner and Haschek,† Berndt,‡ Damarçay,§ and Runge.‖

Between these observers, however, there are great discrepancies, lines given by one being absent in other lists, and the wave-lengths even of strong lines varying between wide limits. Being in possession of perhaps the purest radium hitherto employed for spectrum work, I have used some of it in photographing its ultra-violet spectrum. The negatives so obtained have enabled me to get measurements from which the wave-lengths of the lines have been calculated with an accuracy only limited by the accuracy of the iron lines used us standards.

The spectrograph itself is a five-prism quartz instrument which I have had in use since 1894. A general idea can be gained of the arrangement of the spectrograph from the accompanying outline plan (Fig. 1). The light from the source *a*, passes first through the condenser, *b*, on to a slit, *c*, thence to the collimating lens, *d*, and round the train of prisms, *e*. It then passes through the camera lens, *f*, whence it falls on the sensitive film in the holder, *g*. The whole apparatus is mounted on a planed cast-iron table, *h*, *i*, *j*, *k*, 49½ inches long, 31 inches wide, and 1¼ inches thick. The prisms, lenses, and photographic film-holder are enclosed in a large wooden framework, *l*, *m*, *n*, *o*, *p*, *q*, *r*, *s*, having aluminium shutters on each side, so that the inner adjustments can be effected easily. The height of the enclosure is 28 inches, and the whole is perfectly light-tight when the shutters are down. Outside the dark enclosure, in the space *h*, *l*, *s*, *r*, are situated the arrangements for producing the light to be examined, the optical condensers, and the slit.

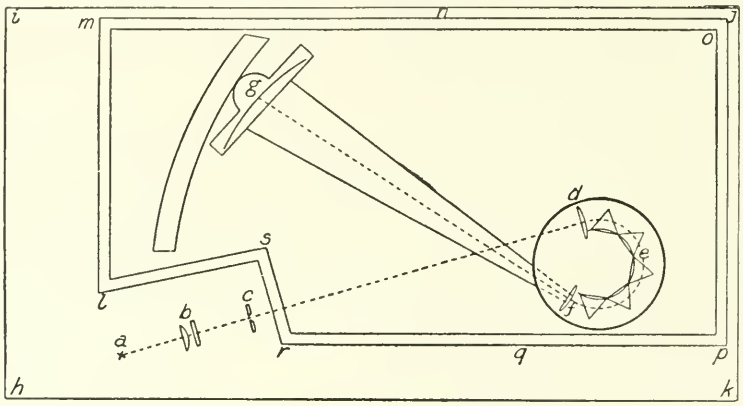


Fig. 1.

An electrical condenser of 180 square inches is intercalated in the secondary circuit, and a coil of twelve turns of well-insulated wire, each turn being 12 inches in diameter, is interposed in the path of the secondary current. This introduction of self-induction in the circuit suppresses most of the air lines, and gives the metal lines on a black background.

The optical efficiency of a spectrograph depends in no small degree on the way in which the source of light is presented to the slit. If the electrodes are too far apart there is distortion, owing to each pole forming its own luminous centre, and if the spark is close to the slit we have to contend with other irregularities; the image is not clear, and the lines are often confused and blurred. If the spark is moved away from the slit the spectrum gains in definition; the greater the distance between the light and the slit the finer is the sharpness and definition of the lines, but at the same time the loss of light is great. This loss of light, however, may be obviated in great measure with considerable improvement of the definition by inserting optical condensers between the spark and the slit. I use two condensers of quartz, plano-cylindrical, one being double the focus of the other, the axes intersecting each other at an angle of 90°; the object being to concentrate a line instead of a point of light on the slit. All optical condensers waste much light. I use them more to obtain well-defined images than to abridge the time of exposure.

The slit is made of two shallow-angled quartz prisms, as I have already described (Chemical News, vol. lxxi., p. 175, April 11, 1895; *Roy. Soc. Proc.*, vol. lxv., p. 241), and the distance apart of the jaws is generally 0·01 m.m.

The quartz prisms, of which there are five, are of 60°, made in two halves of 30° each, according to Cornu's plan, one half being right-handed and the other half left-handed. The contact surface of both bisects the refractive angle of the entire prism, and is placed perpendicularly to the crystalline axis of both prisms. In this way duplication of lines is avoided.

The sensitive film-holder must be set at an angle varying with the portion of the spectrum being photographed, as the focus of the less refrangible is longer than that of the more refrangible rays. Moreover, the focal plane is not flat, so the film itself must follow the diacaustic curve, or the lines on it will not all be in focus together (Chem. News, vol. lxxii., p. 87, August 1895; and vol. lxxiv., p. 259, November, 1896; *Proc. Roy. Soc.*, vol. lxv., p. 242). For this reason glass plates cannot be used, and celluloid films are employed.

To obtain the best definition of any desired line for measurement, expose for a long time and develop briefly, using plenty of potassium bromide in the pyro developer. It is impossible to photograph properly the whole spectrum with a single exposure, so as to have it well defined in all parts, since the brightest lines are over exposed and blurred sideways before the faint ones are impressed. This important fact is too generally lost sight of in spectrum photography.

For correct determination of wave-lengths, it is necessary to photograph on the same film the spectrum of a metal whose lines are known. I generally use iron for this purpose; it has the advantage of giving a large number of very fine lines, the wave-lengths of which have been accurately measured, and not being very volatile the poles do not rapidly wear away. By means of diaphragms

* A Paper presented to the Royal Society, August 1, 1903.

† Franz Exner and E. Haschek, *Wien Akad. Sitzber*, vol. cx., July 1901; Chem. News, vol. lxxxvi., p. 247.

‡ G. Berndt, *Physikalische Zeitschrift*, 2 Jahrg., No. 12; Chem. News, vol. lxxxiii, p. 77.

§ Demarçay, *Comptes Rendus*, vol. cxxix., p. 716; vol. cxxxi., p. 258.

‖ C. Runge, *Astrophysical Journal*, vol. xii., p. 1.

Wave-lengths of the Radium Lines according to different Authorities.

Runge.	Demarçay.	Exner and Haschek.	W. Crookes.	Intensity.	Remarks.
		2512·46			I cannot see this line on my photographs.
			2709·06	20	This is close to an iron line, 2709·14.
		2736·2			I cannot see this line on my photographs.
		2813·60	2813·876	30	Comes between a fine pair of platinum lines.
		2816·25			Probably a platinum line, 2816·1.
		2831·98			I cannot see this line on my photographs.
		2877·10			Probably an iridium line, 2877·1.
		2908·0			Probably a platinum line, 2908·1.
		2976·17			Probably a platinum line, 2975·9.
		3079·97			Probably a platinum line, 3079·8.
		3126·53			I cannot see this line on my photographs.
		3541·77			Ditto.
3649·77	3649·6	3649·33	3649·712	70	A very strong radium line.
			3809·393	10	A faint radium line.
			3812·170	5	A faint radium line.
3814·591	3814·7	3814·62	3814·661	100	The strongest line in the radium spectrum.
		3861·77			I cannot see this line on my photographs. Exner and Haschek include it in their radium lines, but in a note say it is not a line of radium.
			3961·627	5	A faint radium line.
		3993·25			Probably a barium line, 3993·69.
			4010·397	10	A faint radium line.
		4053·81	4053·124	10	A faint radium line.
4341·0	4340·6		4340·619	5	A faint radium line.
	4364·2				I cannot see this line on my photographs.
4436·45	4436·1				Probably a platinum line, 4437·5.
	4458·0				Demarçay says this is the centre of a nebulous band, which begins at 4463·7, has a maximum from 4453·4 to 4455·2, and ends at 4390·0. I cannot see this on my photographs.
4533·33	4533·5				I cannot see this line on my photographs.
	4600·3				Demarçay says (with a query) that this line does not belong to radium. I cannot see it on my photographs.
	4627·4				Demarçay says this is the centre of a nebulous line, which begins sharply at 4621·9, has a maximum at 4627·5, and ends about 4631. I cannot see it on my photographs.
	4641·9				I cannot see this line on my photographs.
4682·346	4683·0	4682·41	4682·149	25	A strong radium line.
	4692·1				I cannot see this line on my photographs.
	4699·8				Ditto.
	4726·9				Ditto.
		4781·4			Ditto.
4826·14	4826·3		4825·896	15	A strong radium line.
5813·9			5813·9		This is a strong citron line, outside the range of my photographs.

close to the slit the experimental and the standard spectra are photographed on the same film, overlapping for about 1 m.m. in the centre (*Roy. Soc. Proc.*, vol. lxv., p. 243). The photographs are then transferred to a measuring machine, and from the figures thus obtained the wave-lengths are calculated.

The radium was used in the form of nitrate, a well-crystallised salt easily soluble in water. The induction spark was taken between platinum poles partly immersed in a strong solution of the salt. On this account the nitrate was used in preference to the chloride. Much platinum is always dissolved when the poles are sparked in a solution of a chloride, while with nitrates this does not occur to the same extent.

The solution was strong, and slightly acid with nitric acid. Many forms of spark tube were tried before a satisfactory form (shown in Fig. 2) was devised. A B is a tube of hard Jena glass with a bulb at the lower end. At the bottom of the bulb a platinum wire is sealed in, and in the upper part of the tube, at B, a short piece of tube is ground in to form a stopper. A long platinum wire passes through from this stopper, bare at the upper part, and guarded with glass inside the bulb tube. A hole, c c, is made at one side of the bulb to form a window, and a piece of platinum tube is put round the lower platinum wire at D, so that its upper end is about 3 m.m. above the end of the wire it surrounds, and a millimetre below the centre of the window, c c. The upper wire should be about 1 m.m. from the top of the platinum tube surrounding the lower wire. Any solution put in the lower part of the bulb is sucked up by capillarity to the top of the platinum tube, and an induction spark between the two wires gives a spectrum of any metal in solution. When exposures of more than ten minutes or so are required, it is necessary to introduce fresh solution to keep the level in the bulb constant. This is easily done during the exposure by means of a small pipette. The splash of the spark throws drops of liquid for some distance, and the heat and decomposition cause nitric acid to come off. These are objectionable when falling on delicate apparatus, and they cause great waste of solution, which with rare bodies is to be avoided; to prevent this a branch tube is sealed in near the top of the spark tube, dipping to the bottom of a flask through a cork. Another tube passes just through the cork, and is connected with an aspirator. During the sparking operation a rapid current of air is drawn in through the window, and all splashes and vapours are washed through the water in the wash-bottle. Thus the acid fumes are kept from injuring the apparatus, and the valuable salt is saved in the wash water.

The presence of platinum lines is due to the platinum poles between which the spark is taken. They are easily identified by photographing a platinum spectrum and a platinum-radium spectrum on the same plate, slightly overlapping one another. The platinum being common to both, gives continuous lines across the two spectra, while the radium lines only appear in one spectrum. Radium

being purified from barium by a tedious process of fractional crystallisation of the bromides is almost certain to show barium lines in its spectrum. I have only been able to use about a grain of perfectly pure radium bromide, all other samples containing traces of barium.

Owing to the length of the spectrum and the necessity of having the lines near the position of minimum deviation to get the greatest sharpness, each photograph is limited to a small extent of spectrum, and eight exposures are needed to take in the whole ultra-violet spectrum, and as far into the visible part as the plates are sensitive to.

The accompanying table gives the wave-lengths of all the lines ascribed to radium by different observers. Many of the early observations are necessarily imperfect, owing to the enormous difficulty of preparing radium compounds of sufficient strength to show a photographed spectrum. And when sufficient concentration was obtainable, the observations were necessarily limited owing to the minute amount available rendering verification difficult.

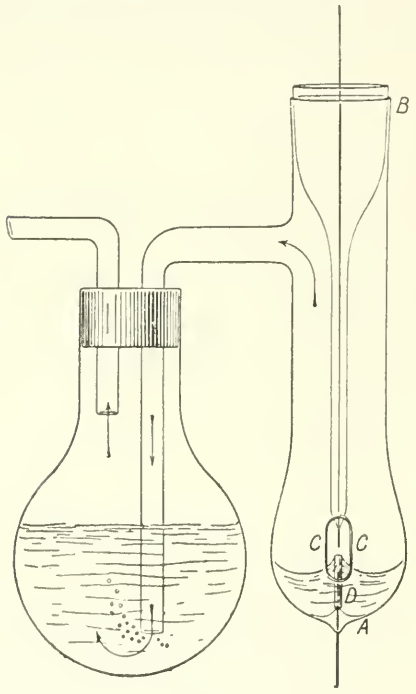


FIG. 2.

Measurements are taken of the exact distances apart of the radium lines and certain adjacent iron lines used as standards. By using a formula, first communicated to the British Association by Sir George Stokes, the wave-lengths of the unknown lines can be calculated. At the time the formula was given it was sufficiently accurate for the instrumental means employed for photographing spectra, but the formula only gave approximate results, and the accuracy of determination of wave-lengths has since improved so much that a correction is required to the original formula. Sir George Stokes, before whom I placed the difficulty in June, 1895, quickly solved it in a satisfactory manner. The usual formula requires the positions of two standard lines of known wave lengths, n_1 and n_3, on each side of the unknown line, n_2. To make the small correction, Sir George advised me to take a third line of known wave-length, chosen well removed from the selected known lines n_1 and n_3. If chosen in the interval 1—3 it had better not be greatly distant from the middle. There is, however, very wide latitude of choice in this respect. All these lines must be photographed and measured in the usual way. Calculate the approximate wave-length of the unknown line by the original formula, and then calculate the approximate wave-length of the third known line by the same formula, *as if it were unknown*, using the two original standards for this purpose also. We have now the approximate wave-length of a known line, as given by the formula, and also its true wave-length. The difference between these two values leads (see below) to the correction to apply to the approximate value of the unknown line.

It often happens that four or more lines are well placed for use as standards. If any three of these be taken, and from them the positions of the other lines be calculated, it will sometimes be found that there is a small residual error in some of them. In such a case the error can be minimised by adjusting the value of the three primary standards so that the sum of the errors on all the lines is a minimum, and in no individual case is very great. Then, with these three corrected standards, the unknown lines may be calculated with confidence to seven figures.

With few exceptions my standards are the most recent published by Rowland. He has given two sets of "Standard Wave-lengths," one in "Astronomy and Astrophysics," vol. xii., p. 321, published in 1893; the other in the *Astrophysical Journal*, vol. i., No. 1, January, 1895, to vol. v., No. 3, March, 1897, and vol. vi., No. 5, December, 1897. Any systematic or accidental error found to occur in Rowland's figures will require a corresponding correction of my own wave-lengths. Assuming Rowland's wave-lengths to be correct, I can follow his seven-figure standards with a probable error of $\pm 0{\cdot}002$ at the most refrangible end, and one of $\pm 0{\cdot}01$ at the least refrangible end. The average error being $\pm 0{\cdot}005$. But on the assumption that all Rowland's measurements are incorrect by a variable amount, as rendered probable by the recent work of Fabry and Perot (*Comptes Rendus*, May 28, 1901, vol. cxxxii., No. 21), a correction will have to be made which will affect the sixth figure.*

For the reduction of the lines 4682·149 and 4825·896, there being no well-defined iron lines suitable for measurement, I have used some strong zinc and cadmium lines, which also have been measured by Rowland.

The following is the method of calculation I now employ:—

n_1 λ_1
n_2 λ_2
n_3 λ_3
n_4 λ_4

n_1 and n_3 are scale positions on the measuring machine of standard lines of known wave-lengths, λ_1 and λ_3.

n_2 is the scale position of the line whose wave-length is required (λ_2).

n_4 is the scale position of an additional standard line whose wave-length is known. It is used for obtaining the correction to apply to the approximate wave-length of λ_2.

E_2 and E_4 are the calculated errors obtained for λ_2 and λ_4, which have to be added to or subtracted from λ_2 or λ_4 to get them accurate.

For the tedious calculations involved in the reduction of the wave-lengths I am indebted to my son, Mr. Bernard H. Crookes, M.Sc.

Rule.

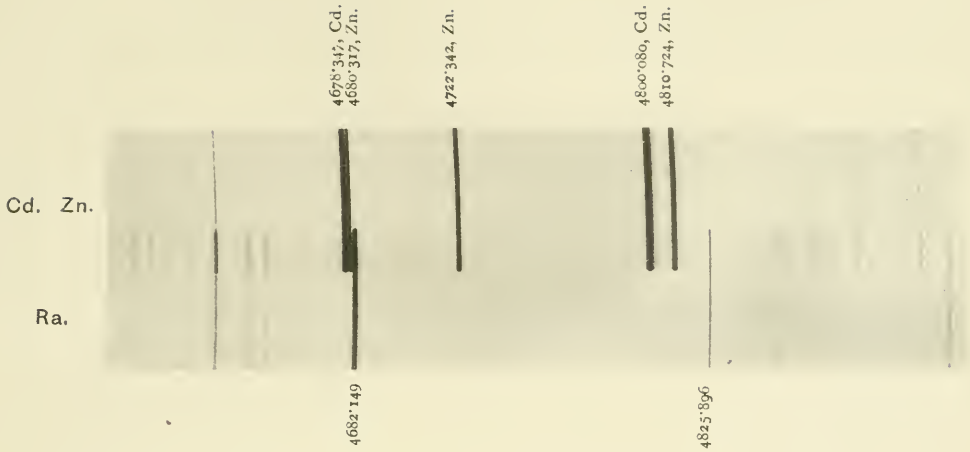
First calculate the approximate value of λ_2 by the following formula:—

$$\frac{\lambda_3^2\lambda_1^2(n_3 - n_1)}{\lambda_1^2(n_2 - n_1) + \lambda_3^2(n_3 - n_2)} = \lambda_2^2 \text{ (approx.)} \quad . \quad . \quad (1).$$

Next, in a similar way, find the approximate value of λ_4, using the following formulæ:—

$$\frac{\lambda_3^2\lambda_1^2(n_3 - n_1)}{\lambda_1^2(n_4 - n_1) + \lambda_3^2(n_3 - n_4)} = \lambda_4^2 \text{ (approx.)} \quad . \quad . \quad (2).$$

* Measuring a ruled glass micrometer in my measuring machine I find the average of ten scale readings can be relied on as not more than 0·00002 inch in absolute error on an average, with occasional errors of double this amount, and of course many errors of less, or zero. The effect of an error of this magnitude represents an error of 0·0025 in the wave-length at one end of the spectrum, and one of 0·011 at the other end.



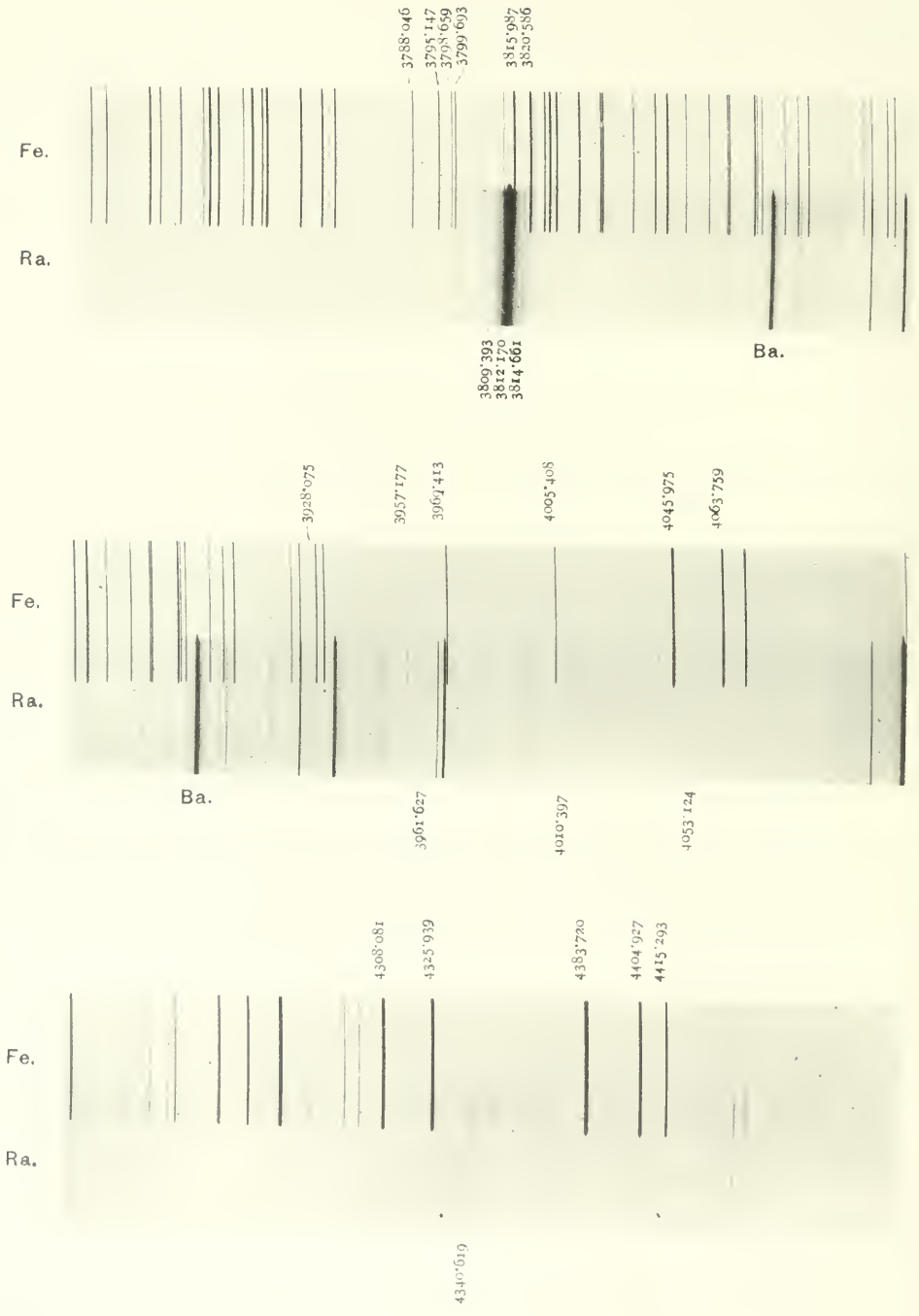
THE ULTRA-VIOLET SPECTRUM OF RADIUM.

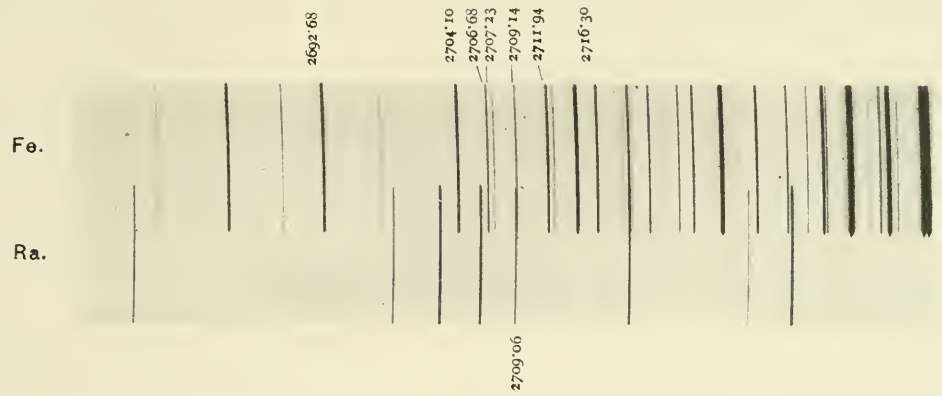
The Collotype illustrations are from the original negatives, and are entirely untouched. The grain of the process somewhat diminishes the sharpness of the lines.

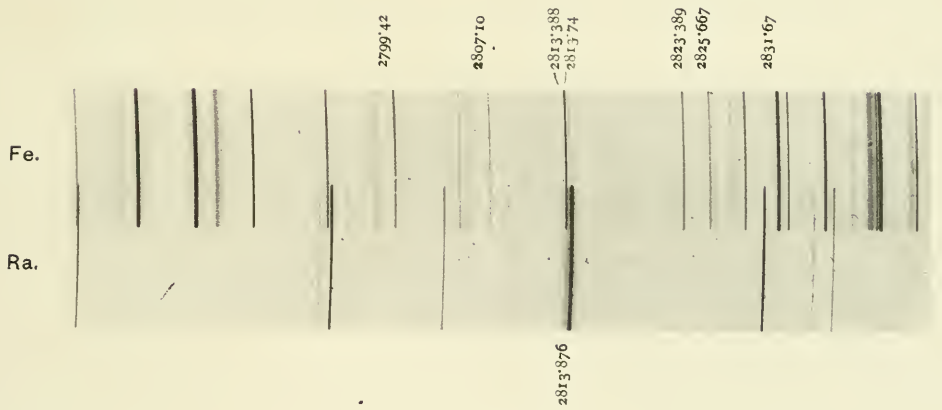
To economise space and avoid unnecessary complications, I have given photographs of only that part of the spectrum adjacent to the radium lines. Had the whole spectrum been given as photographed, the length would have extended to more than 10 feet.

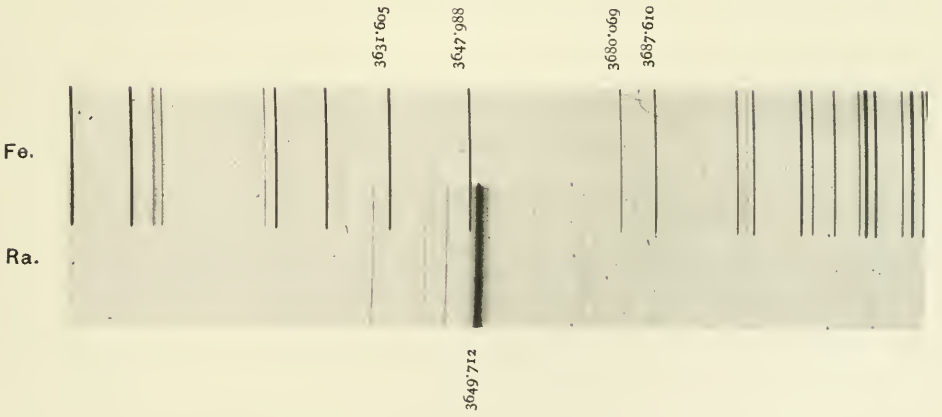
The upper half of each strip shows the iron lines used as standards, with their wave-lengths according to Rowland's latest measurements. The lower halves contain the radium lines, with their wave-lengths as calculated from the iron standards. The other lines on the lower halves are chiefly platinum lines. On the 4th and 5th photograph a strong barium line is shown at wave-length 3891·97 (Rowland), or 3892·42 (Exner and Haschek).

In the part of the spectrum shown on the last strip there are no iron lines suitable for standards. Here, therefore, I have used some good lines of zinc and cadmium the wave-lengths of which are given in Rowland's latest table.


3788·046
3795·147
3799·693
3815·987
3820·586
Fe.
Ra.
3809·393
3812·170
3814·661
Ba.
3928·075
3957·177
3969·413
4005·408
4045·975
4063·759
Fe.
Ra.
Ba.
3961·627
4010·397
4053·124
4308·081
4325·939
4383·720
4404·927
4415·293
Fe.
Ra.
4340·619


2692·68
2704·10
2706·68
2707·23
2709·14
2711·94
2716·30
Fe.
Ra.
2709·06


2799·42
2807·10
2813·388
2813·74
2823·389
2825·667
2831·67
Fe.
Ra.
2813·876


3631·605
3647·988
3680·069
3687·610
Fe.
Ra.
3649·712

Then—

$$\lambda_4 \text{ (true)} = \lambda_4 \text{ (approx.)} \pm E_4.$$

Now calculate E_2 by the following equation :—

$$\frac{\text{(Approx.) } \lambda_2{}^3(n_2 - n_1)(n_3 - n_)}{\text{(Approx.) } \lambda_4{}^3(n_4 - n_1)(n_3 - n_4)} E_4 = E_2 \quad . \quad . \quad (3).$$

Then—

$$\text{(Approx.) } \lambda_2 \pm E_2 = \lambda_2.$$

[In fact, writing y for λ^{-2}, of which the refractive index is a function, and x for n, the graph of the relation between y and x may in this neighbourhood be identified with a parabola. The formulæ (1) and (2) neglect the effect of its curvature, by taking the points 2 and 4 to be on the chord connecting the points 1 and 3. The corrections E_2 and E_4 are thus connected with the distances from the points on this chord to the true points on the curve by the formula $\delta y = -2E/\lambda^3$; and the formula (3) connecting them is the expression of a well-known geometrical property of a parabola].

Example.

Calculate a radium line from adjacent iron lines as standards.

$n_1 = 0{\cdot}000000$. $\lambda_1 = 2813{\cdot}388$ (Rowland).
$n_2 = 0{\cdot}005310$. $\lambda_2 =$ A radium line.
$n_4 = 0{\cdot}107143$. $\lambda_4 = 2823{\cdot}389$ (Rowland).
$n_3 = 0{\cdot}131020$. $\lambda_3 = 2825{\cdot}667$ (Rowland).

2 log λ_1	$\bar{6}{\cdot}8984593$	2 log λ_3	$\bar{6}{\cdot}9022420$
log 0·00531	$\bar{3}{\cdot}7250945$	log 0·125710	$\bar{1}{\cdot}0993698$
log 42029·46	$4{\cdot}6235538$	log 1003718·32	$6{\cdot}0016118$
		42029·46	
		log 1045747·78 =	$6{\cdot}0194269$

2 log λ_3	$\bar{6}{\cdot}9022420$
2 log λ_1	$\bar{6}{\cdot}8984593$
log 0·131020	$\bar{1}{\cdot}1173376$
log numerator	$12{\cdot}9180389$
log denominator	$6{\cdot}0194269$
	2) $6{\cdot}8986120$
	$3{\cdot}4493060 = \log 2813{\cdot}883 = \lambda_2$ (approx.)

2 log λ_1	$\bar{6}{\cdot}8984593$	2 log λ_3	$\bar{6}{\cdot}9022420$
log 0·107143	$\bar{1}{\cdot}0299638$	log 0·023877	$\bar{2}{\cdot}3779798$
log 848053·20	$5{\cdot}9284231$	log 190643·44	$5{\cdot}2802218$
		848053·20	
		log 1038696·64 =	$6{\cdot}0164887$

log numerator	$12{\cdot}9180389$
log denominator	$6{\cdot}0164887$
	2) $6{\cdot}9015502$
	$3{\cdot}4507751 \log 2823{\cdot}418$ = (approx.) λ_4

But— $\lambda_4 = 2823{\cdot}389$
$\therefore$ $E_4 = 0{\cdot}029$

3 log λ_2	$10{\cdot}3479$	3 log λ_4	$10{\cdot}3523$
log 0·005310	$\bar{3}{\cdot}7251$	log 107143	$\bar{1}{\cdot}0300$
log 0·12571	$\bar{1}{\cdot}0994$	log 0·023877	$\bar{2}{\cdot}3780$
log numerator	$7{\cdot}1724$		$7{\cdot}7603$
log denominator	$9{\cdot}2979$	log 0·029	$\bar{2}{\cdot}4624$
	$\bar{3}{\cdot}8745$		$9{\cdot}2979$

$\therefore$ $E_2 = 0{\cdot}007$
$\lambda_2 = 2813{\cdot}876$

EXPERIMENTS AND OBSERVATIONS WITH RADIUM COMPOUNDS.*

By WILLIAM ACKROYD, F.I.C., F.C.S.

The telluric distribution of radium is 0·0003 when gold = 1 (*B. A. Report*, 1902, p. 581; Chemical News, lxxxvi., 187). It has therefore the claim to be regarded as the rarest element known at present. The effects produced by rays from its compounds simulate those of heat to a certain degree, as will be seen in the following account of my experiments and observations, which include some results of a negative character because of their probable bearing on the problem of the origin of the energy of these compounds.

Phosphorescence.

Attention was early turned to observations with diathermanous common salt, NaCl, under the influence of radium rays. Sealed glass tubes containing 5 m.grms. of the pure radium bromide were used, unless otherwise stated. Such a tube resting in common salt produced marked phosphorescence, which lasted for hours after the removal of the exciting cause (Ackroyd, *Nature*, July 23, 1903). A two minutes action of the phosphorescing salt on a photographic plate resting over but not in contact with it, was apparent on development. Slides of the photographic effects are shown of :—(1) A radium bromide tube, with two minutes exposure. (2) The radium bromide tube plus the sodium chloride in which it was imbedded ; two minutes exposure. (3) Sodium chloride alone after excitation for some hours with radium bromide ; thirty minutes exposure. On the first slide is also shown the photographic action of a tube of radiferous barium chloride, to which reference is made later ; its radio-activity compares favourably with that of the 5 m.grms. of pure radium bromide.

The table-salt experimented with was of slightly alkaline reaction to red litmus-paper, and contained traces of the usual impurities. The compound was therefore prepared (1) by precipitation with hydrochloric acid from its solution in distilled water, filtering, drying, and igniting ; and (2) by the neutralisation of caustic soda with hydrochloric acid. In each case the sodium chloride obtained became phosphorescent under the radium bromide rays. Sodium chloride, with a trace of moisture in it, gave better results than the compound kept carefully dry in a desiccator after ignition ; the difference in this respect was very striking on comparison of the phosphorescence of ignited and unignited salt two hours after removal of the radium bromide tubes. The sodium chloride also exhibited phosphorescence when moistened with hydrochloric acid a little over normal strength. The simulation of heat effects becomes apparent on comparing these results with hitherto recorded observations, Sir David Brewster observed phosphorescence when solution of common salt was poured into a cup of heated iron (Blackie's "Pop. Ency.," xi., 49), and Phipson records that common salt is phosphorescent only at a temperature of about 200° C. ("Phosphorescence," p. 20).

Lithium chloride prepared from the carbonate and then fused and ground up into a fine powder exhibited phosphorescence ; when, however, the moisture present (absorbed from the atmosphere in twenty-four hours) became excessive, it ceased to phosphoresce in radium bromide rays.

Potassium chloride phosphoresced under the influence of the rays, but there appeared to be no notable phosphorescence on their removal. The after-phosphorescence of potassium bromide was plainly visible ; negative results were obtained with sodium and potassium iodides. It is interesting to note that in the phosphorescence of the halides of the metals of the alkalis induced by radium rays there is *decrease* with increase of atomic weight ; whereas, with metals of the alkaline earths insolation in effective radiant energy produces an *increase* with increase of atomic weight. These remarks are based on a comparison of the

* A Paper presented to the British Association (Section B), Southport Meeting, 1903.

extreme members of each series, so far as they have been experimented with, and take no account of possible variations in the intermediate members.

The phosphorescence observations were made in a dark room after the eyes had adapted themselves in every case to the absence of light and had attained the necessary degree of sensitiveness to very faint lights.

Colour Change.

Sodium chloride is changed in a few hours from white to orange or buff colour; the freshly ignited salt appeared somewhat pinker in tint. Moistening with hydrochloric acid did not appear to interfere with the change. No colour change was observed with lithium chloride. The absence of change in the lithium salt, the change in the sodium compound, and the order of change in the latter case are all colour facts of somewhat the same character as those I have grouped under the term metachromatism,* where inorganic bodies are changed in colour in the order of the meta-chromatic scale under the influence of sensible heat, and where the tendency to change is least evident in the lightest members of a comparable group. There is the difference, among others, however, that here the changes are more isomeric in their nature, as they appear to last for some time in dry compounds. On the other hand, there may be rapid reversion to the original colour in moist compounds. Thus in potassium chloride made by neutralising caustic potash with hydrochloric acid, crystallising, and then draining, we get crystals of an acid reaction which readily turn from white to violet under radium bromide rays, and on removal of the radium bromide regain the white colour in less than a minute. A similar reversion was observed in moist acid sodium chloride, whereas the dry compound took many days to regain its original whiteness when exposed to daylight. Where change is effected by radium rays the colours produced remind one forcibly of the colours of flowers and of De Candolle's division of them, for they divide themselves into xanthic and cyanic series. The only member of the blue or cyanic series so far discovered is the one which has been variously termed violet, purple, or amethyst. Here there is a striking difference between these phenomena and those of metachromatism. In the latter, all known white compounds which change colour do so to yellow or the xanthic series only; with the changes of white bodies effected by radium rays the new colour may belong to either class.

Bicarbonate of soda is changed to amethyst colour in twenty-four hours, and the same change is exhibited by meta-bisulphite of potash. The Curies discovered that soda-glass is changed from colourless to violet, a change which Becquerel further observed is accelerated by a temperature of 100° C. The French observers have attributed the alteration to the presence of manganese. In this connection it is of interest to note that the violet colour of the amethyst has also been usually attributed to the presence of a small percentage of an oxide of manganese; a reason has been assigned in which this compound plays no part (*vide* Watts's "Dict. of Chem.," v., 1). It appears to me not improbable that in these cases we have physical colour changes of the same kind as that of the bicarbonate of soda, a view which is strengthened by the chemical analogies existing between the compounds of carbon and silicon as contiguous members of the same periodic group, and by the extreme ease and quickness with which the violet glass is made to revert to its original colourless condition at a high temperature.

The various colour changes mentioned in this section were effected in the dark room by imbedding the radium bromide tube in the compound experimented with.

Other Heat Relations.

The Curie demonstration of the evolution of heat by radium compounds has been effected by bringing the substance into surroundings of lower temperature. I have attempted to reverse the conditions. A radium bromide tube was enclosed in a paper cylinder which had been painted with one of Meusel's sensitive colour-changing compounds, preferably the yellow Ag_2HgI_4. It was argued that in a medium of gradually rising temperature the heat from the radium compound within, plus the heat from without, would cause the transition colour change of the paper to be observed earlier in those parts in contact with the radium salt than in those not in contact. The paper cylinder and its enclosed tube were put inside a dry test-tube, which was introduced into a beaker of warm water at or near the transition temperature of the mercury salt; the temperature of the water in the beaker was slowly and gradually raised; the effect looked for was not obtained. Among the reasons that may be given for this negative result is the one that the radium compound was drawing its energy from an external source during the gradual rise of temperature, and therefore behaved no differently from a blank. This is in keeping with Becquerel's observation of the accelerating influence of a rise of temperature on the colour-changing power of rays from a radium compound acting on its glass envelope.

In further repetition of this experiment an endeavour was made to eliminate the glass by emptying a quantity of radiferous barium chloride direct into one of the coloured paper cylinders. The same negative result was obtained. Here the fact was discovered incidentally that the mixture of radium and barium chlorides in such a moist atmosphere lost its power of phosphorescing and of inducing phosphorescence in barium platinocyanide. Numerous attempts to revivify it by chemical means failed, and only ignition in a platinum crucible restored its original qualities (compare F. W. Branson, *Nature*, July 30, 1903). This fact destroys the contention that nothing can be done to a radium compound to diminish or destroy its radio-activity, and it appeared of such importance that it has been several times repeated. In one of these experiments freshly ignited radiferous barium chloride was divided between two tubes and sealed off; both exhibited the quality of continuous phosphorescence in a dark room day after day. The end of one was now drawn out, and water admitted by the capillary thread. With the introduction of moisture the phosphorescence practically ceased. No such result was obtained with a tube of pure radium bromide similarly treated as the phosphorescence after the introduction of distilled water was apparently undiminished. The explanation I advance in the former case is that the water and barium chloride absorb the obscure radiant energy coming from surrounding bodies, which otherwise would have been communicated to the radium compound to make it phosphoresce. It may be mentioned here that moist barium chloride alone gave negative results in radium bromide rays, or, in other words, it is a non-phosphorescent substance.

The following is now suggested as the explanation of *one* of the causes of the continuous phosphorescence of radium compounds. The salts of the metals of the alkaline earths are notably phosphorescent under the influence of suitable exciting rays, and the phosphorescence lasts for hours after insolation; compounds of radium, as the end member of the series, possess the property in an increased degree, and their phosphorescence lasts very much longer still. The cause in the latter case—external radiant energy—is a periodically recurring one, and the excited phosphorescence produced by its absorption lasts longer than the interval between two periods of excitation, and therefore appears continuous. Radium compounds are thus energy transformers to an abnormal degree. Only an effective sifter of the external energy which affects them can stop their manifestations. Ice and most bodies appear to be more or less transparent to this form of radiant energy; the most effective sifters remain to be discovered, and will probably consist for the most part of non-phosphorescent halides.

* Chemical News, vol. xxxiv., p. 75.

THE THEORY OF DYEING.*

By G. von GEORGIEVICS.

The author gives a brief historical introduction to the subject of tinctorial chemistry, and observes that the study of this branch of applied science has been greatly complicated by the publication of large masses of incompletely observed facts. He further remarks that practical unanimity prevails as to the nature of the dyeing process in so far as concerns the application of colours such as chrome yellow, nitraniline red, and the mordant colours; these colours, or compounds of the colours with the mordant, are deposited as such upon the fibre.

The theories, or more properly the hypotheses, concerning the nature of dyeing refer more particularly to the so-called substantive colours; that is, to dyeing with acid colours, basic colours, and direct colours. The principal theories of the process of dyeing are two in number; namely, (1) the chemical theory, and (2) the mechanical theory. In accordance with the first, the dyeing of wool and silk with acid and basic colours is due to the formation of chemical compounds between the colour and the fibre; the chemical combination is supposed to be of a loose, salt-like nature, because the combined colour exhibits a chemical behaviour identical with that of the free colour. The chemical theory offers no plausible explanation of dyeing with direct cotton colours.

The mechanical theory describes the process of dyeing as one of absorption or of solution. Some writers attempt to compromise by describing the dyeing process as partly chemical and partly mechanical in nature, whilst others are of the opinion that the dyeing changes in character with the dye-stuff and the fibre.

In discussing what is required of a theory of dyeing the author states the view that such a theory can be nothing more nor less than an expression of all the hitherto known facts concerning the process. The supporters of the mechanical theory of dyeing do not deny the possibility of the existence of chemical combination, more especially as all colours are of acid or of basic nature, and the animal textile fibres, at least, are not chemically indifferent; they claim, however, that the existence of such a chemical combination has not been hitherto proved in any single case, whilst all the observed facts tell in favour of the mechanical theory. The supporters of the chemical theory of dyeing put forward, as specially important pieces of experimental evidence, two statements, both made by E. Knecht, the one referring to the dyeing of basic colours on wool and silk, the other to dyeing with acid colours. In accordance with the first statement, wool and silk play the part of acids towards basic colours, and the corresponding coloured compounds must be regarded as salts of the colour with keratin or fibroin respectively, because in such dyeing processes the acid is quantitatively split off from the colouring matter, and only the colour base is taken up by the fibre. It is further suggested that the colourless rosaniline base can only give rise to the fuchsin red colour by formation of a salt.

Since this time, however, the author has shown that in dyeing chemically indifferent substances, such as glass and china-clay, which cannot play the part of acids, the acid of the basic colour remains quantitatively in the dye-bath; he has further shown that the rosaniline base exists in a coloured form. The full force of this contradiction of the chemical theory is not fully admitted, it having been objected that many kinds of glass are slightly attacked by water and are thus not chemically indifferent. The author showed many years ago, however, that this objection is founded upon a total disregard of the fact that the results are of a quantitative nature. The author remarks that whilst the attack has been directed against the strong part of his work, its weak point—which is as follows—has not hitherto been noticed. The fact that in the dyeing of chemically indifferent substances with basic colours the acid part of the latter remains quantitatively in the bath is only a proof that one has to deal with the same phenomenon which is observed in the dyeing of silk and wool, and is not an indication that salt formation has taken place between the colour base and the fibre substance; the dyeing of glass and china-clay is, at any rate, a process of absorption, and its external similarity with the dyeing of silk and wool with the same colours is not necessarily a proof of the identity of the two processes. The author's work was directed solely against the validity ascribed to the argument repeatedly brought forward in support of the chemical theory, and still leaves open the question of the nature of the process concerned in the dyeing of animal fibres with basic colours. Should it ever be possible to prove the existence of chemical compounds between colour and fibre it will be most probably done in the case just referred to, but such information could certainly not be obtained in the manner only lately attempted by Knecht. Knecht boiled out with alcohol wool and silk dyed with night-blue, and believed himself forced to the conclusion that the extract contained chemical compounds of the night-blue base with keratin or fibroin respectively. If the conclusion were correct, it would be possible by prolonged repetitions of the operations of dyeing and extraction with alcohol to bring about a gradual destruction of the fibre. The improbability of this is obvious, and the author clearly proves the incorrectness of Knecht's final conclusions by a repetition of the work upon which they are based. After precipitating the colour base and eliminating the alcohol, Knecht prepared aqueous solutions from the above mentioned alcoholic extracts, which, according to his statement, possessed the property of precipitating magenta and night-blue, and which he therefore suppposes to contain keratin or fibroin respectively, or chemical compounds formed from these two substances during the process of dyeing. On repeating these experiments the author finds that the solutions, if perfectly pure fibre material purified with alcohol has been used, precipitate solutions of magenta only, and that but very slightly indeed. The same precipitate may, however, be obtained if silk and wool are left entirely out of the experiments; he finds that by precipitating the colour base from an alcoholic solution of night-blue with barium hydrate, and by afterwards removing the latter from the solution, a liquid is finally obtained which has the property of precipitating magenta. In this instance it is naturally quite out of the question that keratin or fibroin play any part in the precipitation.

The second principal support upon which the chemical theory rests has also been given by Knecht. It was observed at an early date that molecular proportionality between colour and fibre seems non-existent in dyeing trials; the results thus differ from those obtained in cases of ordinary chemical combination. By dyeing wool in very concentrated solutions of picric acid and similar acid colours, Knecht supposed that he had established the existence of chemical compounds formed in definite molecular proportions. The repetition of these experiments by Perger and Ulrich has, however, shown that Knecht in his desire to make the fibre take up as large a quantity of the colour as possible, used such an excess of colour that part of it was deposited as crystals upon the dyed fibre. It is therefore clear that under such conditions it is absolutely impossible to ascertain, even with a small degree of accuracy, the amount of colour which has been actually taken up by the fibre.

The author considers himself justified in stating that these two fundamental supports upon which the chemical theory of dyeing rests cannot withstand any searching criticism.

A considerable number of facts have accumulated during recent years which tend to strengthen the view that the processes of dyeing are uniform and of a mechanical nature. The author showed in 1894 that, in dyeing silk with indigo-disulphonic acid, the distribution of the colour

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

between the residual solution and silk dyed in it is governed by a law which may be expressed by the formula—

$$\frac{\sqrt{C\ \text{solution}}}{C\ \text{fibre}} = K;$$

in which C refers to the concentration of the colour solution, and K is a constant independent of the concentration. Later experiments have shown that this law of the distribution of the colour is applicable to dyeing on silk and wool of other acid colours, and also to the dyeing of direct colours (salt colours) on cotton. It is thus proved, first, that the processes of dying with the acid colours on the one hand and with the direct cotton colours on the other, are identical in kind, and, secondly, that these processes cannot be of a chemical nature. If a chemical compound were formed, the distribution of the colour between the two media would be of an entirely different character, just as Walker and Appleyard have recently indicated. The author has only lately shown that picric acid and oxyazobenzene are deposited on the fibre in a free state during dyeing with these colours; this seems to be of special importance in the case of picric acid. In view of Knecht's statement, and of the fact that picric acid forms compounds with such great readiness, chemical combination, if at all possible, might have been expected in this instance.

Binz and Schroter have lately endeavoured to show that dyeing with oxyazobenzene differs materially from that of the other acid colours. On account of the fastness exhibited by dyeings with oxyazobenzene these authors assumed that this colour forms a stable compound with the substance of the wool as the result of condensation.

As regards the dyeing of acid colours on animal fibres and that of the direct cotton colours on cotton we may therefore safely say that we possess distinct proof that these processes are identical and of a mechanical nature.

The further questions as to whether substantive dyeings should be considered as solid solutions or as resulting from adhesion is still open for speculation.

A STUDY OF MAGNESIUM AND MANGANOUS HYDROXIDES AND OF BARIUM SULPHATE WITH RESPECT TO THE PHENOMENA OF ADHESION AND OF SOLUTION.*

By HARRISON EASTMAN PATTEN.

(Concluded from p. 196).

Manganous Hydroxide.

Method.—The general method used in this investigation was the same as for chromium and iron. The sulphur trioxide was determined directly in "totals" and "filtrates" after the manganese had been removed. This removal was effected in the following manner:—Sodium acetate solution was added to the "filtrates" and "totals," and the manganese precipitated as MnO_2 by bromine, the excess of bromine boiled off, and the MnO_2 filtered off, well washed, and ignited and weighed as Mn_3O_4. The filtrate from this MnO_2 was concentrated, and the SO_3 determined as $BaSO_4$. In the case of the "totals," re-solution of the manganous hydroxide was effected with hydrochloric acid just before the sodium acetate was run in. Occasionally the barium sulphate determinations showed a slight colouration, but the quantity of manganese present was of course negligible. I found this method efficient. Re-solution of these complex precipitates of chromium, iron, manganese, zinc, and aluminium, in hydrochloric or nitric acid, has in every case proved sufficient to split them into determinable components.

The chlorine was determined in presence of manganese, a re-solution with nitric acid being first effected, and then all manganese was washed out of the silver chloride by a wash-water containing 25 c.c. concentrated nitric acid and 0·1 grm. silver nitrate per litre.

Solutions.—A. 98·9 grms. $MnCl_2+4H_2O$ was dissolved in water, and made up to 500 c.c. at 20° C. This solution was found to contain the equivalent of 0·05186 grm. MnO per c.c. B. A solution of potassium hydroxide containing 0·02705 grm. KOH per c.c. at 20° C. C. A solution of sulphuric acid containing 0·04046 grm. per c.c. at 20° C.

Experiments I., II., III., IV., V. were made as shown in Table II. Each system contained 50 c.c. manganous chloride, Solution A; 44·24 c.c. sulphuric acid, Solution C, neutralised to potassium sulphate by 75·63 c.c. of potassium hydroxide, Solution B; and varying amounts of potassium hydroxide to cause the precipitation. In every case the potassium sulphate was run into the flask; next the manganous chloride; and, finally, the potassium hydroxide. Then the system was made up to 500 c.c. at 20° C., and well shaken, whereupon four 50 c.c. portions were drawn out with a pipette, and labelled "totals." The remaining precipitate and solution were thrown upon a dry filter-paper, the filtrate received in a dry flask, and brought back to 20° C., when four 50 c.c. portions were drawn off, and labelled "filtrates." Throughout the investigation of chromium, manganese, and magnesium the same pipette was used.

Discussion.

For results see Table II.; also curves 7 and 8 in the plate. The chemical nature of adhesion is clearly shown here as well as in the case of iron, zinc, chromium, and aluminium. Experiment I. shows no sulphur trioxide in the precipitate, though the mass of precipitate is a maximum. Experiment II. shows that 15·34 per cent of the total sulphur trioxide is in the precipitate, while the mass of precipitate is some 9 per cent less than in Experiment I. Experiment III. shows 19·3 per cent of the total sulphur trioxide in precipitation, while the mass of precipitate is still less than in Experiment II. Experiment IV. confirms Experiment III., giving the maximum sulphur trioxide carried down. Experiment V. shows a falling off in the sulphur trioxide in precipitation, but if we remember how small the amount of precipitated manganous hydroxide is at this point (0·5 molecule KOH) the strength of the action is seen to be considerable.

No chlorine was carried down at 1·5 or 1·1 molecules of KOH; hence this "adhesion" is seen to be selective—the sulphur trioxide is taken, and the chlorine left.

I think it probable that in absence of sulphur trioxide the chlorine would be carried down, since ferric hydroxide shows this same selective action, and does carry down chlorine in absence of sulphur trioxide.

Since in the case of iron, potassium appears in a precipitate only at 8 molecules of potassium hydroxide, and in the case of chromium, potassium does not appear at all up to 8 molecules of potassium hydroxide, it was considered unnecessary to determine potassium in the present investigation.

In the plate, I have plotted curves which show the per cent of oxide and of sulphur trioxide in the precipitates obtained by adding various amounts of potassium hydroxide to the chloride. Ordinates are in per cent of constituent; abscissæ, in molecules of potassium hydroxide required to produce the precipitate. Curve 1 is the per cent of total sulphur trioxide in the precipitate of ferric hydroxide; curve 2, the same for chromic hydroxide; curve 3, the same for ferric hydroxide—produced from a solution of ferric chloride having twice the concentration of that used for curve 1—(curves 1, 3, and 5 are taken from the thesis of V. J. Hall, *loc. cit.*). Curve 7 is the same for manganous hydroxide. Curve 4 gives the per cent of total chromium trioxide precipitated by varying amounts of potassium hydroxide in presence of a fixed amount of potassium sulphate. Curve 5 is the same for ferric oxide. Curve 6, the same for magnesium oxide—presence or absence of potassium sulphate has no effect on the trend of the curve. Curve 8, the same for manganese oxide. Curve 9, the same for zinc oxide

* From the *Journal of the American Chemical Society*, vol. xxv., No. 2.

(C. E. Linebarger, *Journ. Am. Chem. Soc.*, 1895, xvii., 358). Curve 10 is the per cent of total sulphur trioxide in the precipitate whose remaining constituent is aluminium trioxide, the per cent of which is given in curve 11 (taken from Table VI., A. V. E. Young, *loc. cit.*).

My results as plotted in curve 7 show that the action of manganous hydroxide in carrying down sulphur trioxide into precipitation is truly chemical in nature, since the maximum carrying-down effect is observed far short of the maximum quantity of manganous hydroxide, as may be seen by reference to curve 8. The carrying down of chlorine and of potassium oxide remains to be investigated.* The results show, too, that the standard equations for the reaction between manganese chloride and potassium hydroxide, and between magnesium chloride and potassium hydroxide in aqueous solution, do not represent the facts (see curves 6 and 8; likewise, 9 and 11). The distribution of the constituents of these systems is dependent upon temperature, concentration, and the relative masses of the constituents. Further, the composition of the precipitates as given in the tables and curves considers the precipitate as anhydrous; unquestionably much water is combined in the gelatinous precipitates here studied, but owing to the lack of a method of getting at it quantitatively it has purposely been left unconsidered.

This work has a bearing on the subject of colloidal solution. Reference to a former paper will show that it is possible to form a colloidal solution containing chromium chloride, potassium chloride, and potassium hydroxide all combined with each other, and with water, so that the equation $2CrCl_3+3KOH = CrCl_3+Cr(OH)_3+3KCl$ does not represent the true state of the system. If any soluble sulphate be added, this colloidal solution gelatinises. A nitrate or chloride will not produce this effect. It seems to me that this reaction disposes of the idea which had been advanced that *any electrolyte* will precipitate a colloid ("Chromic Hydroxide in Precipitation," *loc. cit.*). Here certainly the colloid seems to have a decided preference for sulphates.

Barium Sulphate.

To examine further this "adhesion" phenomenon, samples of barium sulphate were prepared in two ways:—(1) Precipitated with sulphuric acid from barium chloride dissolved in water, and the washed barium sulphate boiled for several hours with the aqueous solution of some metallic chloride. (2) Precipitated with sulphuric acid from an aqueous solution of barium chloride containing the same metallic chloride used in Method 1.

These samples enable one to decide whether the colouration of barium sulphate which is observed in samples precipitated in presence of salts of iron, manganese, chromium, &c., is necessarily enclosed when the crystal forms.

In this way I prepared samples of barium sulphate containing nickel, cobalt, manganese, chromium, iron, and copper, and examined them under a high-power microscope. The crystals were measured by a stage and eye-piece combination micrometer, and averaged 0·00005 to 0·000125 inch in diameter.

No difference in shade could be detected between barium sulphate crystals prepared by Method 1 and those obtained by Method 2 with any of the metals used. The colouration was well marked, and was compared with that of freshly prepared pure barium sulphate on the same glass side.

These results indicate that the metals given can penetrate barium sulphate crystals after they are formed, and find lodgment there. But once these metals are in the barium sulphate crystal it is, as every analyst knows, no easy matter to get them out. From this we might, without doing violence, argue for chemical combination between the barium sulphate and the metal (or its salt or oxide).

* This work was done in 1896 and I have kept it back, hoping to make the data more complete; however, circumstances have not permitted of it, and do not at present. These results are of interest to those working on precipitation and solution, so I do not feel justified in withholding them longer.

TABLE II.

Experiment.	$KOH+\frac{1}{2}K_2SO_4$.	"Total" MnO.	"Filtrate" MnO.	"Precipitate" MnO.	"Total" SO_3.	"Filtrate" SO_3.	"Precipitate" SO_3.	"Total" Cl.	"Filtrate" Cl.	"Ppt." Cl.	Total SO_3 in "precipitate." Per cent.	Total MnO in "precipitate." Per cent.
I.	2	0·2593	0·0146	0·2347	0·1381	0·1379 0·1368	0·0000	—	—	—	—	90·51
II.	1½	0·2593	0·04371	0·2122	0·1382	0·1186 0·1154	0·1170	0·3307	0·0212	0·3335 0·3321	0·0000	15·34	81·83
III.	1⅛	0·2593	0·0833	0·1760	0·1376	0·1110 0·1111	0·1110	0·3298	0·0266	0·3302 0·3340	0·0000	19·33	67·86
IV.	1	0·2593	—	—	0·1384	0·1103 0·1106	0·1104	—	0·0270	—	—	19·50	—
V.	½	0·2593	—	—	0·1378	0·1244 0·1247	0·1245	—	0·0133	—	—	9·65	—

Further, chromic chloride in aqueous solution is known to dissolve barium sulphate crystals in appreciable amount. This shows that we have here a case of mutual action, the barium sulphate dissolving the chromium (in some form), and the chromium chloride in water dissolving the barium sulphate. As the barium sulphate remains solid, we have another case of a solid solution, and a liquid solution coming into equilibrium in such a way as to give ground for believing that solid solution and liquid solution are of the same order, and to be classed as chemical combinations of solvent with solute.

I wish to thank Professor A. V. E. Young, of Northwestern University, for many helpful suggestions given me during the progress of this work.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 12, September 21, 1903.

Properties and Constitution of Manganese Steels.—Léon Guillet.—The author continues his exhaustive study of manganese steels from the mechanical as well as the micrographical point of view. The experiments were performed on two series of very pure steels: the first containing 0·100 to 0·250 per cent of carbon, and the manganese increasing from 0 to 33 per cent; the second series containing 0·700 to 0·950 per cent of carbon, and the manganese varying from 0 to 12 per cent. The results obtained show the perfect coincidence between the metallographical and mechanical experiments. The author further establishes the great similarity existing between manganese and nickel steels. The "shock" experiments show clearly that less carburetted steels, and those containing less than 4 to 5 per cent of manganese, are not at all fragile. In a future paper he hopes to collect the present results in a simple diagram, similar to that obtained in the case of the nickel steels.

MISCELLANEOUS.

Regulations as to Milk-stores and Milk-shops, &c.—At a meeting of the Corporation of London, at the Guildhall of the City of London, on July 23, 1903, it was resolved:—That certain regulations with regard to the purveying of milk be approved and adopted, the said regulations to come into force on September 1st, 1903. The object of these regulations is to prevent the infection and contamination of milk within the City of London, and under them every purveyor of milk, dairyman, or cowkeeper must be registered as such. Rules are laid down with regard to the sanitary conditions of all dairies and cow-sheds, and the prevention of infection from any person engaged in the business, special attention being given to the maintenance of a pure and plentiful supply of water.

Oxidation by means of Fluorine set free by Electrolysis.—F. W. Skirrow.—On contact with water, fluorine produces ozone; in this manner the author has effected different electrolytic oxidations in the presence of dissolved hydrofluoric acid. Sulphate of chromium gave chromic acid; the manganous salts gave permanganates, and the return is much greater than in the presence of sulphuric acid. The salts of cobalt gave the sesquioxide. Experiments made with carbonic and sulphuric acids did not lead to any results. Hydrocarbons, such as benzene and naphthalene, are oxidised energetically in hydrofluoric solution, and more rapidly than in sulphuric solution.—*Zeit. Anorg. Ch.*, vol. xxxiii., p. 25.

The Solubility of Boric Acid in Hydrochloric Acid.—W. Herz.—Contrary to the statements to be found in Dammer's Treatise on Chemistry, boric acid is less soluble in hydrochloric acid than in water. The following determinations were made at 26°. In hydrochloric acid of known strength, boric acid was dissolved until the saturation point was reached, then, on a known volume of the liquor, the total acidity was estimated, after the addition of mannite:—

HCl in molecules per litre.	B_2O_3 in molecule per litre.
0·0	0·907
0·130	0·895
0·260	0·870
0·390	0·842
1·30	0·645
2·16	0·542
4·32	0·308
6·0	0·338
7·08	0·327
8·74	0·327
9·51	0·338

—*Zeit. Anorg. Ch.*, vol. xxxiii., p. 355.

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2292.

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 201).

Chapter III. (*continued*).

Ionising Action of Radium Rays on Insulating Liquids.

M. Curie has pointed out that radium rays and Röntgen rays act upon liquid dielectrics as upon air, imparting to them a certain electrical conductivity. The experiment was carried out in the following manner (Fig. 9) :—

The experimental liquid is placed in a metal vessel, C D E F, into which a thin copper tube, A B, is plunged; these two pieces of metal serve as electrodes. The outer vessel is maintained at a known potential, by means of a

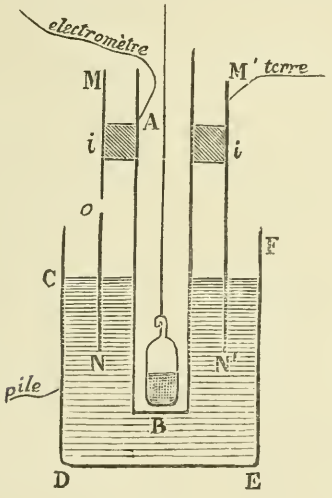


Fig. 9.

battery of small accumulators, one pole of which is connected to earth. The tube, A B, is connected to the electrometer. When a current traverses the liquid the electrometer is kept at zero by means of a quartz electrical piezometer, which gives the strength of the current. The copper tube, M N M' N', connected to earth, serves as a guard tube, preventing the passage of the current through the air. A bulb containing the radium-barium salt may be placed at the bottom of the tube, A B; the rays act on the liquid after having penetrated the glass of the bulb and the sides of the metal tube. The radium may also be allowed to act by placing the bulb beneath the side, D E.

In working with Röntgen rays the course of the rays is through side D E.

The increase of conductivity by the action of the radium rays or the Röntgen rays seems to be produced in the case of all liquid dielectrics; but in order to determine this increase, the conductivity of the liquid itself must be so slight as not to mask the effect of the rays.

M. Curie obtained results of the same order of magnitude with both radium rays and Röntgen rays.

When investigating with the same apparatus the conductivity of air or of another gas under the action of the Becquerel rays, the intensity of the current obtained is found to be proportional to the difference of potential between the electrodes, as long as the latter does not exceed a few volts; but at higher tensions, the intensity of the current increases less and less rapidly, and the saturation current is practically attained for a tension of 100 volts.

Liquids examined with the same apparatus and the same radio-active body behave differently; the intensity of the current is proportional to the tension when the latter varies between 0 and 450 volts, and when the distance between the electrodes does not exceed 6 m.m.

The figures of the following table multiplied by 10^{-11} give the conductivity in megohms per c.c. :—

Carbon bisulphide	20
Petroleum ether	15
Amylene	14
Benzine	4
Liquid air	1·3
Vaseline oil	1·6

We may, however, assume that liquids and gases behave similarly, but that, in the case of liquids, the current remains proportional to the tension up to a much higher limit than in the case of gases. It therefore seemed probable that the limit of proportionality could be lowered by using a much more feeble radiation, and this idea was verified by experiment. The radio-active body employed was 150 times less active than that which had served for the previous experiments. For tensions of 50, 100, 200, 400 volts, the intensities of the current were represented respectively by the numbers 109, 185, 255, 335. The proportionality was no longer maintained, but the current showed great variation when the difference of potential was doubled.

Some of the liquids examined are nearly perfect insulators when maintained at a constant temperature and when screened from the action of the rays. Such are liquid air, petroleum ether, vaseline oil, and amylene. It is therefore very easy to study the effect of the rays. Vaseline oil is much less sensitive to the action of the rays than is petroleum ether. This fact may have some relation to the difference in volatility which exists between these two hydrocarbons. Liquid air, which has boiled for some time in the experimental vessel, is more sensitive to the action of the rays than that newly poured in; the conductivity produced by the rays is one-fourth as great again in the former case. M. Curie has investigated the action of the rays upon amylene and upon petroleum ether at temperatures of $+10°$ and $-17°$. The conductivity due to the radiation diminishes by one-tenth of its value only, in passing from 10° to $-17°$.

In the experiments in which the temperature of the liquid is varied, the temperature of the radium may be either that of the surrounding atmosphere or that of the liquid; the same result is obtained in both cases. This leads to the conclusion that the radiation of radium does not vary with the temperature, and remains unaltered even at the temperature of liquid air. This fact has been verified directly by measurements.

Various Effects and Applications of the Ionising Action of the Rays Emitted by Radio-active Substances.

The rays of the new radio-active substances have a strongly ionising action upon air. By the action of radium *the condensation of supersaturated water vapour* can be easily induced, just as happens by the action of cathode rays and Röntgen rays.

Under the influence of the rays emitted by the new radio-active substances, the *distance of discharge between two metallic conductors for a given difference of potential is increased;* to put it otherwise, the passage of the spark is facilated by these rays.

In causing conductivity, by the action of radio-active bodies, in the air in the neighbourhood of two metallic conductors, one of which is connected to earth and the other to a well-insulated electrometer, the electrometer is seen to be

* Thesis presented to the Faculté des Sciences de Paris.

permanently deflected, which gives a measure of the electromotive force of the battery formed by the air and the two metals (electromotive force of contact of the two metals, when they are separated by air). This method of measurement was employed by Lord Kelvin and his students, the radiating body being uranium; a similar method had been previously employed by M. Perrin, who was using the ionising action of Röntgen rays.

Radio-active bodies may be employed in the study of atmospheric electricity. The active substance is enclosed in a little box of thin aluminium fixed at the extremity of a metal wire connected with the electrometer. The air is made to conduct in the neighbourhood of the end of the wire, and the latter adopts the potential of the surrounding air. Radium thus replaces, with advantage, the flames or the apparatus of running water of Lord Kelvin, till now in general use for the investigation of atmospheric electricity.

Fluorescent and Luminous Effects.

The rays emitted by the new radio-active bodies cause fluorescence of certain substances. M. Curie and myself first discovered this phenomenon when causing polonium to act upon a layer of barium platinocyanide through aluminium foil. The same experiment succeeds yet more easily with barium containing radium. When the substance is strongly radio-active the fluorescence produced is very beautiful.

A large number of bodies are capable of becoming phosphorescent or fluorescent by the action of the Becquerel rays. M. Becquerel studied the effect upon the uranium salts, the diamond, &c. M. Bary has demonstrated that the salts of the metals of the alkalis and alkaline earths, which are all fluorescent under the action of luminous rays and Röntgen rays, are also fluorescent under the action of the rays of radium. Paper, cotton, glass, &c., are all caused to fluoresce in the neighbourhood of radium. Among the different kinds of glass, Thuringian glass is specially luminous. Metals do not seem to become luminous.

Barium platinocyanide is most conveniently used when the radiation of the radio-active bodies is to be investigated by the fluoroscopic method. The effect of the radium rays may be followed at distances greater than 2 m. Phosphorescent zinc sulphide is made extremely luminous, but this body has the inconvenient property of preserving its luminosity for some time after the action of the rays has ceased.

The fluorescence produced by radium may be observed when the fluorescent screen is separated from the radium by absorbent screens. We were able to observe the illumination of a screen of barium platinocyanide across the human body. However, the action is incomparably greater when the screen is placed immediately in contact with the radium, being separated from it by no solid screen at all. All the groups of rays appear capable of producing fluorescence.

In order to observe the action of polonium, the substance must be placed close to the fluorescent screen, without the intervention of a solid screen, unless the latter be extremely thin.

The luminosity of fluorescent substances exposed to the action of radio-active bodies diminishes with time. At the same time the fluorescent substance undergoes a transformation. The following are examples:—

Radium rays transform barium platinocyanide into a brown, less luminous variety (an action similar to that produced by R ntgen rays, and described by M. Villard). Uranium sulphate and potassium sulphate are similarly altered. The changed barium platinocyanide is partially regenerated by the action of light. If the radium be placed beneath a layer of barium platinocyanide spread on paper, the platinocyanide becomes luminous; if the system be kept in the dark, the platinocyanide becomes changed, and its luminosity diminishes considerably. But if the whole be exposed to light, the platinocyanide is partially regenerated, and if the whole is replaced in darkness the luminosity reappears with vigour. By means of a fluorescent body and a radio-active body, we have therefore obtained a system which acts as a phosphorescent body capable of long duration of phosphorescence.

Glass made fluorescent by the action of radium becomes coloured brown or violet. At the same time its fluorescence diminishes. If the glass thus changed be warmed, it is decolorised, and when this occurs the glass becomes luminous. The glass has now regained its fluorescent property in the same degree as before the transformation.

Zinc sulphide, which has been exposed for a sufficient length of time to the action of radium, gradually becomes used up, and loses its phosphorescent property, whether under the action of radium or that of light.

The diamond becomes phosphorescent under the action of radium, and may thus be distinguished from paste imitations, which have only a very faint luminosity.

All the barium-radium compounds *are spontaneously luminous*. The dry anhydrous halogen salts emit a particularly intense light. This illumination cannot be seen in broad daylight, but it is easily visible in the twilight or by gas-light. The light emitted may be strong enough to read by in the dark. The light emitted emanates from the entire body of the product, whilst in the case of a common phosphorescent body, the light emanates specially from the portion of the surface illuminated. Radium products lose much of their luminosity in damp air, but they regain it on drying (Giesel). There is apparently conservation of luminosity. After many years no sensible modification is produced in the luminosity of feebly active products, kept in the dark in sealed tubes. In the case of very active and very luminous radium-barium chloride, the light changes colour after several months; it becomes more violet and loses in intensity; at the same time the product undergoes transformations; on re-dissolving the salt in water and drying it afresh, the original luminosity is restored.

Solutions of barium-radium salts, which contain a large proportion of radium, are equally luminous; this fact may be observed by placing the solution in a platinum capsule which not being itself luminous permits of the faint luminosity of the solution being seen.

When a solution of a barium-radium salt contains crystals deposited in it, these crystals are luminous at the bottom of the solution, and much more so than the solution itself, so that they alone appear luminous.

M. Giesel has made a preparation of barium-radium platinocyanide. When this salt is newly crystallised, it has the appearance of ordinary barium platinocyanide and is very luminous. But gradually the salt becomes spontaneously coloured, taking a brown tint, the crystals at the same time becoming dichroic. In this state the salt is much less luminous, although its radio-activity is increased The radium platinocyanide, prepared by M. Giesel, changes still more rapidly.

Radium compounds are the first example of self-luminous bodies.

(To be continued).

New Publication.—A new journal dealing with chemical and physical science has been brought out recently in Geneva by M. Phillippe A. Guye, Professor of Chemistry at the Univerity of Geneva. The primary object of this new venture is to facilitate the centralised publication of papers on physico-chemical subjects written in the French language, either *in extenso* or in an abridged form. In the second place, a bibliographic bulletin will be given at as early a date as possible, comprising an analysis of all papers on physical chemistry appearing in other languages, all the important works on these subjects published in other countries, and all the patents dealing with the special subjects of this new journal, which will be known as the *Journal de Chimie Physique*.

SILICIDES OF CHROMIUM.

By P. LEBEAU and J. FIGUERAS.

The action of silicon on a metal in the presence of copper has enabled one of us to prepare in a state of purity the definite compounds formed by silicon with iron, cobalt, and manganese. We may mention that this method consists in reacting on a mixture of copper and the metal to be combined, with variable proportions of silicon in the form of silicised copper, free silicon, or of nascent silicon resulting from the action of sodium on an alkaline fluosilicate. Through the application of these different processes to the study of the binary compounds of chromium and silicon, we have succeeded in isolating the following four silicides :—$SiCr_3$, $SiCr_2$, Si_2Cr_3, and Si_2Cr.

The silicide $SiCr_3$ is produced when we fuse a mixture of chromium and copper with a small quantity of silicon. An ingot containing—Cu 85·63, Cr 12·83, Si 1·24, gave, after alternate treatments with nitric acid and dilute soda, a residue consisting entirely of prismatic crystals of the compound $SiCr_3$. In another experiment in which the mass melted had the following composition :—Cu 84·32, Cr 10·83, Si 4·36, this same silicide, $SiCr_3$, still remained perfectly homogeneous after the attack.

Above this proportion of silicon, and with quantities of chromium and silicon very similar in amount, we observe, besides the crystals of $SiCr_3$, other very different crystals, having brilliant facets in the form of a lozenge. They constitute the silicide $SiCr_2$. By the treatment of an ingot containing—Cu 78·22, Cr 12·04, Si 8·92, this compound has been isolated in a very pure state.

In following up the study of the fused products containing increasing quantities of silicon, we find, in the residues, new crystals formed of very brilliant prisms, differing most decidedly from the thickest crystals of $SiCr_3$. With the following proportions :—Cu 83·84, Cr 3·03, Si 12·92, we obtain a very homogeneous residue of long prisms, answering to the formula Si_2Cr_3.

Finally, as the proportion of silicon increases in the products of fusion, we observe the formation of a fourth compound in small crystals of a deep colour and much less brilliant than the preceding ones. Further, these latter disappear completely, and with high proportions of silicon we only find, as a result of the attack with nitric acid, the fourth variety mixed with free silicon, which can be eliminated by means of soda. This body is the chromium compound richest in silicon, and answers to the formula Si_2Cr.

Among these four silicides of chromium two have been described already; the silicide $SiCr_3$ was obtained by M. Zettel (*Comptes Rendus*, vol. cxxvi., p. 833), and the silicide $SiCr_2$ was prepared and examined by M. Moissan (*Ann. Chim. Phys.*, [7], vol. ix., p. 289). As for the compound Si_2Cr, it was announced by M. de Chalmont (*Ann. Chim. Phys.*, vol. xix., p. 69), but this chemist did not succeed in extracting it from the matrix in which it was formed. Only the silicide Si_2Cr_3 is entirely new; we will therefore describe its preparation and principal properties.

Preparation of the Silicide of Chromium, Si_2Cr_3.—It is prepared the most easily by heating in the electric furnace in a carbon crucible, a mixture of 100 grms. of silicide of copper at 12 per cent, with 4 grms. of chromium. The time of heating should be about four minutes, with a current of 600 ampères and 70 volts. The resulting ingot should weigh approximately the theoretical amount. It is broken up and attacked with nitric acid at 50 per cent, taking care to alternate with washings with commercial soda-lye diluted with ten times its volume of water. When these reagents no longer dissolve anything, wash with water and dry in the oven.

The above mixture may be also melted over a forge. The cooling is slower in this case, and much better formed crystals are obtained.

Properties of the Silicide Si_2Cr_3.—The silicide Si_2Cr_3 crystallises in long quadrangular prisms, rarely terminated. Its density at 0° is 5·6. It scratches glass, but will not mark quartz.

Chlorine reacts on this compound at about 400°, giving chromic chloride and chloride of silicon; bromine attacks it more slowly at a cherry-red heat; under the same conditions iodine is without any action.

The silicide of chromium is unoxidisable in the air, either dry or moist, in the cold. At a temperature of 1100° it becomes covered with a very thin iridescent layer which prevents any further action of the oxygen.

Hydrochloric acid gas decomposes it, with the production of chromous chloride. A solution of dilute hydrochloric acid has no action in the cold on this silicide; a concentrated solution dissolves it with the greatest ease if gently heated. Nitric and sulphuric acids are without action, but hydrofluoric acid attacks it almost immediately.

Fused nitrate and chlorate of potassium, both of which react energetically on the carbides of chromium, have no effect on this silicide; on the other hand, with the alkaline carbonates it is rapidly transformed into an alkaline silicate and oxide of chromium. If we add a nitrate, a mixture of alkaline silicate and chromate is formed. This latter reaction, as well as that of hydrochloric acid, has been utilised for its analysis :—

	Found.	Theory.
Si	26·32, 26·81, 26·40	26·65
Cr	74·11, 73·64, 73·33	73·34

It should be remarked that the compounds of chromium and silicon do not show the analogies of formula that one of us has already described for the silicides of iron, cobalt, and manganese. These metals each furnish, in fact, three compounds corresponding to the types—SiX_2, SiX, and Si_2X. With chromium there are certainly the silicides $SiCr_2$ and Si_2Cr, but there are also two bodies with formulæ which are not comparable, viz., $SiCr_3$ and Si_2Cr_3.*—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 15.

PURIFICATION OF THE SULPHURETTED HYDROGEN USED FOR THE DETECTION OF ARSENIC.

By ARMAND GAUTIER.

To precipitate arsenic from its acid solutions in the state of sulphide Selmi used sulphuretted hydrogen produced by the decomposition of the alkaline or alkaline-earthy sulphides by hydrochloric acid.†

I have not specially examined the gas thus produced, having found it more practicable to purify ordinary sulphuretted hydrogen. It always contains arsenic, particularly in the form of arseniuretted hydrogen, resulting from the metal in the sulphide; arseniuretted hydrogen that is not decomposed by sulphuretted hydrogen, and that four or five washings with acid or water will not remove completely. A moderate current of ordinary sulphuretted hydrogen gas washed in this manner, passing a bubble at a time for two hours through nitric acid heated to 80°, gave me 0·08 m.grm., or nearly a tenth of a milligrm. of arsenic.

To purify sulphuretted hydrogen I tried passing the impure gas through a tube heated to dull redness. The arsenic is deposited principally in the front part of the tube, with a little sulphur coming from the sulphuretted hydrogen; but it is not yet pure. It still gives, after passing

* We have extended our researches to the silicised compounds of nickel, but these latter having less resistance to the action of acids their separation is much more difficult. In any case, the series of these silicides seems to be of the same type as that of the silicides of cobalt, manganese, and iron.

† I have observed that sulphuretted hydrogen passed, first hot and then cold, through an arsenical solution containing from 1 m.grm. to 0·002 m.grm. of arsenic, precipitates the whole of this metalloid so completely that the filtered liquor no longer contains the slightest trace.

through warm nitric acid for two hours, a ring of 0·004 m.grm. of arsenic.

For its complete purification, the sulphuretted hydrogen gas, first washed with water, is passed through a vertical column of 30 c.m. of moist pumice stone, then through a combustion-tube filled with fragments of glass and heated to dull redness for a distance of 25 c.m. The gas is then passed through one of my serpentine bulb-tubes filled with a concentrated solution of sulphide of barium, when it again deposits traces of arsenical compounds. Finally, it is passed through a tube packed with cotton-wool before arriving at the liquor in which it is to react. Thus purified, this gas, after a passage, bubble by bubble, through boiling nitric acid, which oxidises the whole, gave me a total amount of arsenic of 0·0008 m.grm. Not a trace could be found when 300 to 400 c.c. of this gas were passed through acidulated water.

If we pass a current of impure sulphuretted hydrogen, simply washed in a series of acid and water bulbs, through an acidulated aqueous solution of 300 or 400 c.c., such as that obtained by treating by my method the azotised carbon resulting from the destruction of organic matter; in this liquor we find, after two hours, from 0·001 to 0·0006 m.grm. of arsenic, instead of the 0·080 m.grm. contained by the whole of the gas as shown above. Impure sulphuretted hydrogen introduces an error of not less than 1 m.grm. in the result—an error which is of considerable magnitude in an estimation of such delicacy.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 16.

TITRATIONS WITH POTASSIUM IODATE.

By LAUNCELOT W. ANDREWS.

As is well known, when potassium iodide is titrated with chlorine water in a neutral solution, the reaction which takes place is expressed by the equation—

$$KI + 3Cl_2 + 3H_2O = KCl + HIO_3 + 5HCl \quad . \quad . \quad (1).$$

On the other hand, it may not be so well known that if a large excess of free hydrochloric acid is present during the titration, chloroform or carbon tetrachloride being used as before for an indicator, the reaction will be—

$$KI + Cl_2 = KCl + ICl. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

In both cases the end of the reaction is shown by the immiscible solvent becoming colourless. If instead of chlorine water we titrate with a solution of potassium iodate, the stage at which the reaction stops is likewise dependent upon the concentration of the acid. If this be low, the reaction goes no further than to set the iodine free in accordance with the equation—

$$5KI + KIO_3 + 6HCl = 6KCl + 3I_2 + 3H_2O \quad . \quad . \quad (3),$$

while if a great excess of hydrochloric acid is present the reaction runs—

$$2KI + KIO_3 + 6HCl = 3KCl + 3ICl + 3H_2O \quad . \quad (4),$$

the immiscible solvent remaining violet in the former case (No. 3), but in the latter becoming colourless, while the supernatant solution turns bright yellow from the iodine chloride. The probable explanation of this behaviour is that iodine chloride, as the salt of a very weak base, undergoes hydrolysis in a neutral or feebly acid solution, with the production of the corresponding hydroxide and acid; thus—

$$ICl + H_2O = IOH + HCl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

the iodous hydroxide ("hypoiodous acid"), which is formed, undergoing spontaneous conversion into iodic acid, &c., whereas the hydrolysis is prevented by a great excess of hydrochloric acid.

The reaction of equation (1) was used long ago by A. and F. Dupré (*Liebig's Ann. Chim.*, 1855, xciv., 365) for the titration of iodides. In order to compare the reactions of the first two equations, I titrated 5 c.c. of a decinormal potassium iodide solution with chlorine water in presence of 5 c.c. of chloroform. After the addition of 75·4 c.c. of the latter the chloroform became colourless. The titration was now repeated with the further addition of respectively 15, 20, and 30 c.c. of strongest hydrochloric acid, and the amounts of chlorine water required were 25·4, 25·22, and 25·25 c.c., the end reaction being of extraordinary sharpness. Nearly three times as much chlorine was therefore required in the absence of hydrochloric acid as in its presence, as the theory demands. Probably, if the small amount of acid produced by the reaction itself (Equation 1) had been neutralised by the addition of calcium carbonate the theoretical amount of 75·75 c.c. of chlorine solution would have been required. In order to judge the influence of smaller quantities of acid, the titration was repeated with addition of 1, 2, 5, and 10 c.c. of concentrated hydrochloric acid, when respectively 34·1, 26·9, 26·0, and 25·6 c.c. of chlorine water were required.

From these preliminary experiments, it appeared that the hydrolysis of the iodine chloride might be wholly inhibited by addition of a sufficiency of acid, and that a solution of potassium iodate might be successfully substituted for the chlorine water, thus realising the reaction of Equation 4. 9·7465 grms. of acid potassium iodate were dissolved in water and made up to 1 litre. According to the theory, each c.c. of this solution should be equivalent to 16·6 m.grms. of potassium iodide. To 10 c.c. of a solution of pure potassium iodide (20·6 grms. to the litre), 5 c.c of chloroform, 20 c.c. of water, and 30 c.c. of concentrated hydrochloric acid (sp. gr. 1·21) were added, and the mixture was titrated in a glass-stoppered bottle of 250 c.c. capacity, with the iodate solution, shaking briskly, until the chloroform lost its colour, the end-point being exceedingly sharp. 12·43 c.c. of the iodate solution were required. Hence, 0·20634 grm. potassium iodide was found against 0·20600 taken, or 100·17 per cent. In a second experiment, 15 c.c. of the iodide solution, titrated in the same way with 33 c.c. of hydrochloric acid and no additional water, required 18·62 c.c. of the iodate solution, corresponding to 0·30900 grm. found, against 0·30900 grm. taken, or 100·00 per cent taken.

The process as described can be applied to the titration of chromates. For this purpose the chromate is added to an excess of a titrated potassium iodide solution, with 5 c.c. of chloroform and sufficient concentrated hydrochloric acid to be at least half the volume of the entire mixture at the close of the titration. The titration is then carried out precisely as described above. In one experiment of this sort, 36·3 m.grms. of potassium pyrochromate were taken, and 36·8 m.grms. found.

The following experiment shows the applicability of the process to the titration of free iodine:—0·3447 grm. of pure iodine was weighed and placed in the stoppered bottle previously used, with 5 c.c. of a potassium iodide solution containing 20·6 grms. per litre; 10 c.c. of fuming hydrochloric acid, and 5 c.c. of chloroform were added, and the titration was carried out in the usual way. Required, 19·85 c.c. of standard iodate. Since 6·20 c.c. are required for the iodide, 13·65 c.c. remain as corresponding to the free iodine, or 0·3467 grm. iodine found; 100·46 per cent.

To determine whether the method can be used for determination of chlorates, and under what conditions, the succeeding experiments were tried. Five c.c. of a solution of potassium chlorate containing 70·3 m.grms. of the pure salt was added to 25 c.c. of the potassium iodide solution mentioned above, and 50 c.c. of fuming hydrochloric acid. After standing fifteen minutes in the stoppered bottle, 5 c.c. of chloroform were added, and the titration completed. Required, 13·65 c.c. of the iodate. As the iodide is equivalent to 31·0 c.c., 17·35 c.c. correspond to the chlorate, whence 70·9 m.grms. of potassium chlorate were found. In a second similar experiment, only 40 c.c. of hydrochloric acid were used, and the mixture was titrated at once, without standing. In this case 13·98 c.c. of iodate were required, hence 69·55 m.grms. of chlorate were found.

This shows, as was expected, that the chlorate must be left for some time in contact with the hydrochloric acid and potassium iodide for the completion of the reaction. In a third experiment, exactly similar to the last except that the mixture was allowed to stand twenty-four hours before titration, 13·77 c.c. of iodate were required, whence 70·41 m.grms. of chlorate were found. It is therefore a matter of indifference whether the time of digestion is a quarter of an hour or twenty-four hours. In a fourth experiment, 5 c.c. of another potassium chlorate solution containing 33·46 m.grms. of the pure salt was allowed to stand for ten minutes with 10 c.c. of iodide solution, and 20 c.c. of fuming hydrochloric acid; then 5 c.c. of chloroform were added, and the titration was performed. Required, 4·23 c.c. of iodate. Calculated for the iodide, 12·40 c.c., whence 33·39 m.grms. of chlorate were found. Other experiments, not necessary to detail, show that there must be a decided excess of iodide as compared with the chlorate; otherwise the results are likely to be a little too low. The necessary working conditions for the titration of a chlorate can be prescribed as follows:—

To the solution of the chlorate, add an exactly known amount of pure potassium iodide (a titrated solution may be used), in a glass-stoppered bottle, and an amount of fuming, pure hydrochloric acid at least one-third greater than the volume of the solution. Close the bottle tightly, and allow it to stand fifteen minutes after shaking, then add 5 c.c. of chloroform. On now shaking, the chloroform must become deep violet. If the colour is pale, an insufficiency of iodide has been added, and it is better to begin again rather than to attempt to bring the analysis into order. Now add the decinormal iodate with intermittent violent shaking until the chloroform becomes colourless, which point can be estimated with the utmost precision. Each c.c. of a decinormal iodate solution is equivalent to 2·782 m.grms. of $(ClO_3)'$.

Solutions of arsenious acid or chloride can be titrated in the same way as iodides, the reaction being expressed by the equation—

$$2AsCl_3 + KIO_3 + 5H_2O = 2H_3AsO_4 + KCl + ICl + 4HCl.$$

In this case, however, unlike the other, a too great concentration of hydrochloric acid must be avoided, since under those conditions the end-point becomes obscure, probably a phenomenon connected with the formation and dissociation of arsenic pentachloride. The suitable concentration of the acid is therefore confined within somewhat narrow limits, but not so narrow as to cause any practical difficulty in working. It was found that 30 per cent of hydrochloric acid, calculated on the weight of the entire liquid at the close of the titration, exceeds the permissible maximum limit, while 25 per cent does not. On the other hand, the minimum limit is in the neighbourhood of 12 to 15 per cent of acid. For the experiments noted below, a solution of sodium arsenite was employed in which the amount of arsenious oxide had been determined by titration with iodine solution in the ordinary way. Taken, 25 c.c. arsenious solution (243·8 m.grms. As_2O_3) and 50 c.c. of fuming hydrochloric acid; required 24·45 c.c. decinormal = 242·1 m.grms. of arsenious oxide. Taken, 5 c.c. arsenious solution, 5 c.c. hydrochloric acid, and 10 c.c. water; required, 4·91 c.c. of iodate = 48·6 m.grms.; found, 48·8 m.grms. by iodine titration. Taken, 20 c.c. arsenious solution and 40 c.c. hydrochloric acid; required, 19·69 c.c. iodate = 194·9 m.grms. arsenious oxide; found, 194·7 m.grms. by iodine titration. Taken, 15 c.c. arsenious solution and 30 c.c. hydrochloric acid; required, 14·79 c.c. iodate = 146·4 m.grms. arsenious oxide; found, 146·3 m.grms. by iodine titration.

To summarise, add to the arsenious solution an amount of fuming hydrochloric acid sufficient to make the hydrochloric acid equal to about 20 per cent of the entire mixture at the end of the titration, and 5 c.c. of chloroform; then run in from a burette as large a proportion as can be judged of the whole amount of decinormal iodate requisite, shake well, and continue titrating with the iodate until the chloroform is colourless. Each c.c. of the stand solution corresponds to 9·9 m.grms. arsenious acid or 7·5 m.grms. arsenic.

The determination of antimony is precisely like that of arsenic. A solution was prepared of pure re-crystallised antimonyl tartrate, containing 31·251 grms. per litre. Twenty-five c.c. of this were mixed with 30 c.c. hydrochloric acid and 20 c.c. water, and titrated as usual. 23·62 c.c. of the iodate were required, equivalent to 784·6 m.grms. tartar emetic found as against 781·3 m.grms. taken. In this determination the amount of hydrochloric acid should have been greater by 15 c.c. In the next experiment, 25 c.c. of the antimonious solution with 25 c.c. of hydrochloric acid required 23·50 c.c. of iodate, equivalent to 780·6 m.grms. of antimony salt found (781·3 taken). Twenty-five c.c. antimony solution with 35 c.c. fuming hydrochloric acid required 23·54 c.c. of iodate, whence is calculated 781·2 m.grms. potassium antimonyl tartrate.

Since copper does not interfere in the least with the application of the method, it is possible, for example, to titrate the arsenic in Paris green directly without preliminary separation. Thus, 20 c.c. of a sodium arsenite solution with 20 c.c. of fuming hydrochloric acid required 8·95 c.c. of iodate, the same, plus 1 grm. of copper sulphate, required 9·00 c.c. of iodate. For the analysis of Paris green, 0·5 grm. of the substance is dissolved in 15 c.c. of water and 25 c.c. of fuming hydrochloric acid, and directly titrated with 5 c.c. of chloroform and the decinormal solution of iodate.

Ferrous salts can be titrated in exactly the same way as iodides. Taken, 2·0874 grms. ammonium ferrous sulphate; required, 26·06 c.c. iodate, equivalent to 297·6 m.grms. iron found, or 14·26 per cent; theory, 14·25 per cent. Unlike the titration with potassium permanganate, oxalic acid does not interfere with this determination. Taken, 2·0843 grms. ammonium ferrous sulphate and 1 grm. oxalic acid; required, 25·95 c.c. iodate, equivalent to 296·3 m.grms. iron, or 14·22 per cent. Ferric salts do not interfere with any of these titrations, nor do bromides to any serious extent, if the amount is small. The end-reaction in the titration of ferrous salts is somewhat slow, and, in spite of the satisfactory results of the test analyses, is lacking in the sharpness that distinguishes the other titrations described in this paper. This difficulty appears to be avoided by the addition of a small amount of manganous chloride, but the point requires further examination.

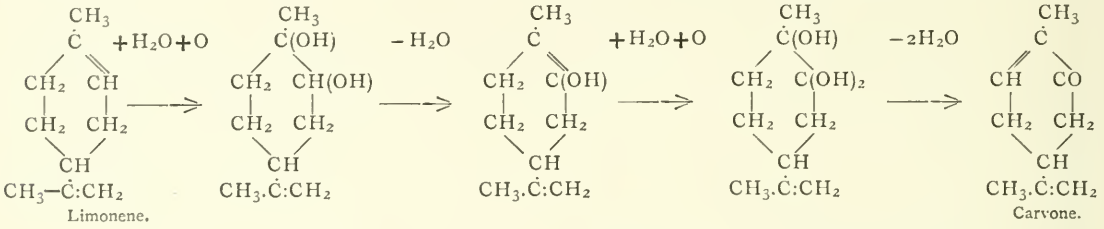
The method which has been described is adapted to the determination of almost all the substances to which Bunsen's process of distillation with potassium iodide and hydrochloric acid is applicable, with at least equal precision, with less expenditure of time and far simpler apparatus. It is furthermore applicable in certain cases in which the Bunsen method is not, as, for example, the titration of arsenic or antimony in the presence of copper and ferric compounds.—*Journal of the American Chemical Society*, vol. xxv., No. 7.

Action of different Metallic Powders on Carbonic Oxide.—Paul Sabatier and J. B. Senderens.—The authors have tried the action of heated nickel, cobalt, and iron in powder on carbonic oxide. They find that, with nickel and cobalt, there is a catalytic decomposition of the oxide of carbon, and this may be explained in several ways. The authors are not of the opinion that the cause can be attributed to a purely physical action of the condensation of the gas, due to the porous condition and the large surface of the metals formed by reduction; platinum-black, which is generally so efficacious, has no action in this case. The cause appears to be, as in most similar phenomena, the formation of temporary, unstable compounds, the intermediate production of which determines the principal reaction.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 8.

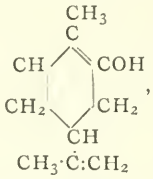
ESSENTIAL OILS.*

By Dr. O. SILBERRAD.

The production of essential oils, although of extreme antiquity, has only recently been made the subject of scientific research. The earlier methods of extraction from the plants were exceedingly crude, and it was only in the early part of the Nineteenth Century that the industry received a new impulse by the introduction of steam distillation for the recovery of these essences. Chemical research has in recent years led to the replacement of the natural oils to some extent by products artificially prepared. As an instance of this, the author's recent discovery that carvone, $C_{10}H_{14}O$, the active principle of carraway oil, could be obtained direct from limonene by autoxidation was referred to. The mechanism of the reaction is probably expressed as follows:—



The above explanation is confirmed by the fact that the author has recently succeeded in isolating a monatomic alcohol as an intermediate product, to which he assigns the formula—



which corresponds to the hitherto unknown carvol. A specimen of the acetate of this alcohol was exhibited.

Other instances investigated by the author are the active principles of ylang-ylang, neroli, carnation, and oil of myrrh.

The specimens shown illustrate how nearly the synthetic products approach to the natural perfumes. A new and much more economical method for the manufacture of terpineol, recently discovered by the author, was briefly referred to. One great advantage claimed for this method was that the ingredients generally considered necessary for the reaction are replaced by much less costly reagents.

The author then went on to consider the various ways of obtaining essential oils, and showed that the methods of extraction differ for the various natural oils.

I. Turpentine, the source of terpineol, is obtained from pine trees in America by the process of "boxing," succeeded by steam distillation. Venetian turpentine is obtained by drilling holes in the trees, whilst Strasbourg and laurentine turpentine is still collected in certain districts by means of small pointed cans.

II. A second method is that of direct distillation from the plant, used, for instance, in the preparation of camphor and the recovery of camphor oil from the wood of *Lauras camphora* in Japan. Further treatment of the distillate leads to its separation into camphor, light camphor oil (mainly pinene, phellandrene, and dipentine), and heavy camphor oil, which latter is interesting as the source of safrol, from which piperonal is now commercially obtained under the name of heliotropine. Investigations by the author have facilitated this conversion of safrol into isosafrol, and very considerably reduced the cost of production of heliotropine.

The conversion of safrol into vanilline by treatment with sodium methylate and subsequent oxidation is also interesting; the chief source of vanilline is, however, eugenol obtained from oil of cloves. Eugenol is associated in oil of cloves with a sesquiterpene cariophyllene from which the author has recently obtained an acid containing eleven carbon atoms. (A specimen of this acid was exhibited).

III. A process of expression is used for the extraction of oils which are decomposed by steam, such as bergamot (linalool acetate). The artificial preparation of this ester presents considerable difficulties, as linalool undergoes decomposition or isomerisation on coming in contact with acids, and gives only very small yields of the desired esters, but investigations by the author have led to its manufacture on a commercial scale. A laboratory method whereby the difficulty may be overcome, worked out by the author, was also described, and consisted in treating a pyridene solution of the alcohol with the required acidyl chloride. The investigation of linalool has hitherto laboured under the difficulty that no solid derivative of this alcohol could be obtained. It is hoped that the author's recent preparation of a crystalline compound of linalool — the hexanitrodiphenylurethane—will be of assistance in this direction. Geraniol, an isomer of linalool, is important as the chief ingredient of otto of roses. Its acetic and butyric esters are also valuable as scents.

A fourth and very ancient method for the extraction of essential oils is illustrated by jasmine oil, which is obtained by exposing the flowers over odourless petroleum, whereby the perfume is absorbed and subsequently extracted with acetone. This oil is a mixture of a number of compounds, the distinctive odour being, however, due to jasmone, which is present to only a small extent in the oil. Peach oil contains also a large number of constituents; among these the author has isolated the ethyl ester of an undecylenic acid, the presence of which is interesting as being a case of the natural occurrence of a fatty acid containing an odd number of carbon atoms.

The sesquiterpene alcohol, santalol from sandal-wood oil, irone from orris oil, the oxygenated products from orange oil, lemon oil, and lime oil were briefly treated of. The specimens of these various compounds illustrated their valuable properties as perfumes. A few brief remarks throughout the paper illustrated the costliness of these oils; thus it was shown that about three tons of roses were required to yield one pound of otto; the cost of peach oil is between three and four times as great, whilst to prepare one pound of jasmone about 200 tons of jasmine flowers would be required.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

Research on the αβ-Dimethylglutaric Acids. — E. E. Blaise.—This research has had a double object—the synthesis of the αβ-dimethylglutaric acids, and the verification of certain theoretical questions as to whether tiglic acid can give synthetically only one racemic or not, the other one being furnished by angelic acid. In the end the author found that, contrary to expectation, both angelic and tiglic acids give the same product of condensation. It must be mentioned, however, that the dimethylglutaric acid obtained from angelic acid appeared to be less pure, and seemed to contain a small quantity of an isomer, probably liquid, and which could not be isolated in the pure state.—*Bull. Soc. Chim.*, S8ries 3, vol. xxix., No. 8.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, ESQ., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, October 10th, 1903.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 211 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 211 samples examined by us during the month, 209 were clear, bright, and well filtered, and two samples were slightly turbid.

The rainfall at Oxford during September shows a deficit. The actual amount of rain measured was 1·54 inches; the average for the month is 2·39 inches, leaving a deficit of 0·85 inch, which, subtracted from the previous excess of 9·77 inches, leaves a total excess for the first nine months of the year of 8·92 inches. This is 49·3 per cent above the average for the past thirty-five years.

As autumn approaches, all natural surface waters, like the supplies from the valleys of the Thames and Lea, begin to show an increased amount of vegetable matter in solution. In spite, however, of there being less rainfall during September, the soluble organic matter has increased, although it still remains below the amount present during the month of June.

Our bacteriological examinations of 369 samples taken during the last month have given the results recorded in the following table. Besides these samples we have examined 418 others from special wells, standpipes, &c., making a total of 787 samples in all :—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	333
New River, filtered (mean of 74 samples) ..	19
Thames, unfiltered (mean of 25 samples).. ..	6202
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 195 samples)	39
Ditto ditto .. .. highest	496
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 24 samples) ..	330
River Lea, from the East London Water Company's clear-water wells (mean of 25 samples)	29

Of the 294 daily samples taken from the filter wells of the Metropolitan Water Companies, seven samples, or 2·4 per cent, were sterile. There were twenty-seven samples, or 9·1 per cent, containing more than 100 microbes, and of these, ten samples contained more than 150 microbes per c.c. The twenty-seven excess samples contained an average of 182 microbes per c.c.; in August thirty-eight excess samples contained an average of 180 microbes per c.c.

The general result of the month's chemical and bacteriological examination is to show that while the organic carbon has increased, the microbic impurities have diminished. Efficient filtration has been well maintained considering the exceptional season.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE COLOURS OF IODIDES.*

By WILLIAM ACKROYD, F.I.C.

THE general law of the relation of colour to chemical constitution was stated by the author in 1892 (CHEMICAL NEWS, 1893, lxvii., 27). Briefly it is that in related compounds of the general formula, A_xB_y, as B increases in weight (either in atomic mass or multiple of atomic mass) there is increase of absorption of light in definite manner, so that the visible effect is progression in the metachromatic scale from the white towards the black end. With one colour vision this would appear like a gradual darkening—an aspect of the phenomenon which the author ("On Opacity to the Röntgen Rays," W. Ackroyd and H. B. Knowles, *Journ. Soc. Dyers and Colourists*, April, 1896, vol. xii.) regards as being presented by X-rays in the photographic effects produced by them after passing through equal thicknesses of the members of a series A_xB_y. That this generalisation is reasonably fact-embracing is seen when it is stated that there are only about 2·27 per cent of exceptions in a survey of some 616 correlated inorganic coloured compounds, and many of these exceptions are of a doubtful nature.

Iodides conform to the law; the more heavily weighted molecules have colours nearer the black end of the scale; while the lighter ones, on the other hand, come nearer the white end. Thus in vertical series of the periodic classification arsenic tri-iodide is orange as compared with the red of antimony and bismuth tri-iodides; magnesium, zinc, and cadmium iodides are white, while mercuric iodide is yellow or red. In the periodic groups there are forty-one examples of iodides; only three are apparently uncomformable, two of these being doubtful exceptions.

When there is more than one iodide of the same metal we have again conformity to rule, thus :—Hg_2I_2 is olive green, and HgI_2 yellow or red.

The iodides have also a normal colour when compared with the other halides of the same radical as in the series AsF_3, $AsCl_3$, $AsBr_3$, and AsI_3. In the tabulation of these relations conformity to the law is seen both in horizontal as well as vertical groups, and 270 colour facts are presented in such a tabulation which give less than 3 per cent of exceptions.

Finally, the result of recent research shows that the element iodine has also a normal colour among the other liquid and solid halogens; their absorption increases from fluorine to iodine through the extremes of white to black.

It is amply apparent, therefore, that in a comparable series of compounds having similar molecular structure as represented by the same general formula, we may have colourless or white bodies at one end and coloured substances at the other end. Hence it is contended that Professor H. E. Armstrong's view that colour is an indication of "quinonoid" structure does not hold for iodides as maintained by Miss I. Smedley (*Brit. Assoc. Report*, 1902, p. 582), nor for inorganic bodies generally.

Tables are given illustrating these various observations.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

SYNTHESIS OF GLUCOSIDES.*

By W. SLOAN MILLS, M.A., Queen's College, Glasgow (1851 Exhibition Scholar).

The first known instances of the synthesis of a glucoside occurring in nature was effected by Michael, who, having prepared helicin from acetochloroglucose and sodium salicylic aldehyde in absolute alcohol solution, reduced it with sodium amalgam, and obtained salicin. Eugenol and phenol glucosides and also methylarbutin were prepared by Michael (*Comptes Rendus*, 1879, lxxxix., 355; and *Am. Chem. Journ.*, v., 6, 336). His method was somewhat modified by Ryan (*Journ. Chem. Soc.*, 1899, lxxv., 1054), who prepared *o*- and *p*-cresol gluosides, and also carvacrol glucoside, which contains an unchanged phenolic hydroxyl group. Glucosides of the alcohols and mercaptans have been prepared by Fischer (*Ber.*, 1893, xxvi., 2400; 1894, xxvii., 674, 2483, 2985) by the action of the alcohol or mercaptan on the sugar in presence of hydrochloric acid. A series of crystalline α- and β-acetochloro and acetobromo glucoses have recently been obtained by Fischer and Armstrong (*Ber.*, 1901, xxxiv., 2885), by which the synthesis of many alkyl and phenol glucosides has been effected. They have also prepared acetodibromoglucose, which Professor Fischer allowed me to use with a view to preparing glucosides containing a bromine atom in the glucose rest, and also amidoglucosides.

Preparation of Phenolbromoglucoside, $(C_6H_7O.(OH)_3.Br.O.C_6H_5)$.

A solution of potassium phenolate in absolute alcohol was allowed to act on a solution of acetodibromoglucose in chloroform for fourteen days. The solution was filtered, and the residue obtained on spontaneous evaporation was neutralised with acetic acid and extracted with ether. When the ether was evaporated a residue was obtained which, when re-crystallised from dilute alcohol, gave beautiful white needle-shaped crystals of phenolbromoglucoside, melting at 165° C. The glucoside reduces Fehling's solution. It is easily soluble in ether, acetone, and ethylacetate, soluble in alcohol, and somewhat soluble in chloroform. It is easily soluble in concentrated sodium hydroxide, and the solution, when carefully neutralised, gives a precipitate which melts at 170—180° C., and which reduces Fehling's solution only after being hydrolysed by boiling with dilute acids. The bromine in phenolbromoglucoside is not precipitated by silver nitrate solution.

It is hoped to replace the bromine atom in this compound by an amido group, and then by splitting off the phenol rest to obtain an amidoglucose, and thus determine tho position of the second bromine atom in acetodibromoglucose.

PRELIMINARY NOTE ON SOME ELECTRIC FURNACE REACTIONS UNDER HIGH GASEOUS PRESSURES.*

By J. E. PETAVEL and R. S. HUTTON.

An account was given of work carried out in the electrochemical laboratory at Owens College with an inclosed electric furnace constructed to work with gaseous pressures up to 200 atmospheres. The power employed has been usually about 15 kilowatts per hour, the furnace containing a charge of about 20 lbs. of material, and 1000 to 2000 litres of gas. A second furnace of about one-tenth the capacity was used for gas reactions with high-tension current.

The reactions at present under investigation include the direct reduction of alumina by carbon, the condition of formation of calcium carbide, particularly as modified by the change of gaseous atmosphere, and the formation of graphite. With regard to gaseous reactions a study of the production of nitric acid and cyanogen compounds has already been commenced.

The preliminary experiments have shown that under pressure alumina is reduced to the metallic condition, but in all cases accompanied by a large amount of aluminium carbide. This reaction is most unfavourably influenced if the carbon monoxide which is formed be retained, whereas it is favoured by the rapid removal of the gaseous products of reaction. So far as calcium carbide is concerned, contrary to expectation, the yield is in no way diminished by the presence of carbon monoxide gas even at high pressures. An important difference in the methods of working is necessary in those cases where it is desired to effect purely gaseous reactions. Here a high-tension current is required. For instance, the formation of nitric acid, even at pressures of 100 atmospheres, is only accomplished in appreciable amount where the electromotive force used is of several thousand volts.

A general description was also given of the plant employed for preparing and compressing the various pure gases required in quantity for this work.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

NOTE ON THE RATE OF COMBUSTION AND EXPLOSIVE PRESSURE OF CORDITE.*

By J. E. PETAVEL.

The research of which a preliminary account was given is being carried out in the physical laboratories of the Owens College.

The subjects under investigation are :—The effect of the diameter of the cordite, of the charging density, and of the shape of the enclosure.

The curves of rise and fall of pressure are for each explosion automatically recorded; the high pressure recorder described at a previous meeting being used for this work (see *Report Brit. Assoc.*, Glasgow, 1901, p. 768; and *Phil. Mag.*, May, 1902).

Attention was drawn to the dangerous vibrations which are set up when the charge is not uniformly distributed throughout the enclosure.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

Action of Boiling Caustic Lyes on Picric Acid.—E. Wedekind and J. Haeussermann.—It has been observed some time ago that picric acid or its salts, by the action of boiling alkalis, undergo decomposition to a more or less considerable extent; that on boiling a solution of picrate of barium in caustic baryta hydrocyanic acid is formed, and that solutions of picric acid in an excess of alkali give off a small quantity of ammonia. The authors have endeavoured to follow up and define these reactions; they have observed that on heating for eight hours with a large excess of soda, potash, or baryta lye there is about 5·9 per cent of ammonia formed, or decidedly less than one molecule. When the solution is made acid a slight odour of hydrocyanic acid is observed; this proves that a small portion of the nitrogen has escaped transformation into ammonia. Further, a considerable amount of oxides of nitrogen is formed, which shows that the alkaline picrates heated in the presence of an excess of alkali give rise to the formation of alkaline nitrate, as suspected by the authors. They have shown, by estimations of the NO, that a nitro group of the picric acid is eliminated in the form of nitrite, and that the action of the above three lyes is quantitatively different, contrary to what was found in the estimation of the ammonia. After having eliminated the oxide of nitrogen, the authors have not been able to isolate from the product of the reaction, which is a solid homogeneous substance, anything else than unchanged picric acid in small quantities. The chemical reaction involved is probably very complicated.—*Berichte*, vol. xxxv., p. 1133.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY OF NEW SOUTH WALES.

General Monthly Meeting, Wednesday, August 5, 1903.

F. B. Guthrie, F.I.C., F.C.S., President, in the Chair.

"*On the Protection of Iron and other Metal Work.*" By William M. Hamlet, F.I.C., F.C.S., Government Analyst.

The author pointed out that the stability and permanence of the materials used in building construction depended on the application of a knowledge of chemistry and physics, and that the engineer, architect, and builder must keep in touch with this knowledge in order to make the best use of the nature and possibilities of their materials; and just as the chemist seeks a knowledge of the structure and disintegration of matter, so also will he know of the best means to adopt for the protection of materials against the wear and tear of atmospheric and other influences. Any given structure, whether it be a ship, an engine, a house, or a bridge, will, if left to itself, become weathered, perish, and decay unless protected. The many hosts to be thus reckoned with are:—Chemical and electrical influences, mechanical and meteoric changes, erosion by sand, wind, and rain, factory chimney emanations, all more or less accelerated by contraction and expansion, together with biological influences and animal depredations.

It is found that by examining the structure of a metal much useful information may be obtained as to its powers of resistance under given circumstances. A section of a metal, for instance, is highly polished and then etched by an acid, an alkali, or a peroxide, either applied directly or by electrolytic methods. From the visible grain, texture, or structure, as seen under the microscope, good and bad materials may be differentiated one from another.

This method of examination and testing materials has come rapidly into use during recent years, and is particularly useful in the case of iron, steel, bronze, brass, Muntz, and other yellow metals.

The rusting of iron and steel is dealt with, the author referring to experiments made from time to time during the last fifteen years, and the immediate cause of the publication of this paper at the present time was owing to a paper published in a recent number of the *Journal of the Chemical Society* by Dunstan, followed by a similar one by Moody on the rusting of iron. The former observer lays stress on the action of hydrogen peroxide, while the latter accounts for rust by the action of carbonic acid, which action he compares to the action of any mineral acid on iron, with the consequent liberation of hydrogen. Petit, in 1896, showed that the mere presence of carbonic acid gave rise to corrosion and formation of ferrous carbonate, which is one of the antecedent products in the formation of rust.

The author was engaged in a work of investigating the causes of the rapid corrosion or rusting away of the iron casing at one of the Australian artesian bores, where abundance of carbonic acid gas was evolved at the rather high temperature of 100° F.; the water also contained alkaline carbonates and bicarbonates with sodium chlorides, silica, &c., amounting to between 30 and 40 grains of total solid matter to the gallon. This is an admittedly difficult case to deal with, and probably a specially hard and resistant alloy will be required to stand the prolonged and severe action of the water in question.

The protection of ironwork under usual conditions is best effected by the use of a paint or an enamel having a coefficient of expansion equal or nearly equal to that of the iron itself, so that cracking or bursting of the skin of paint shall be prevented, which would otherwise lead to exposure of the bare iron to outside influences. Dr. Angus Smith's composition, the Bower-Barff process, red-lead, iron oxide, asphalte, and graphitic paints were each considered, the author holding a high opinion of simple pure red-lead and genuine linseed oil as an excellent covering for most purposes. Galvanised iron, lead, bronze, Muntz metal, and copper were each referred to, especially to the action of the air of towns and manufacturing districts.

NOTICES OF BOOKS

Thermodynamics and Chemistry. A Non-mathematical Treatise for Chemists and Students of Chemistry. By P. Duhem. Authorised Translation by George K. Burgess. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. 8vo. Illustrated. Pp. xxi.—445.

Chemists, especially those engaged in teaching classes in advanced chemistry, will heartily welcome Dr. Burgess's translation of "Thermodynamique et Chimie" by the brilliant Professor of Physics at the University of Bordeaux, M. P. Duhem.

In the United States, the author's eulogistic remarks on the work of the late Prof. J. Willard Gibbs will be read with due appreciation. Prof. Duhem writes:—"Many do not hesitate to compare the illustrious author of the *Phase Law* to our Lavoisier." Elsewhere the French chemist writes of Gibbs's work as the natural continuation of Lagrange's "Mécanique Analytique," and points out the international character of its subsequent development, for it was transformed into chemical theory first in Holland, by van der Waals, Bakhuis, Roozboom, and van 't Hoff, as well as by the labours of Henri Sainte-Claire Deville in France.

In the volume under review the calculus is not used, and the reader is supposed to have no attainments in mathematics and in physics beyond those possessed by the graduate of a good high school.

The first 100 pages deal with the principles of chemical status; after this, the author takes up the phase rule and the philosophy of monovariant and bivariant systems—a classification that he esteems of great utility. Mixed crystals, critical states, the mechanics of perfect gases, chemical dynamics, and explosions, occupy the remainder of the volume.

Three indexes help the reader to find that sought—an index of authors cited, an index of chemical substances studied, and a general index.

In its original language this treatise is already favourably known, in its English dress it deserves a wider acquaintance.

Introduction to the Rarer Elements. By Philip E. Browning. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. Pp. viii.—157. 8vo.

This useful work fills a long-felt want, for larger works on general chemistry cannot give the space to the rarer elements which they deserve, nor indeed are details of these rare bodies needed in works having in view merely instruction.

Since there is no table of contents, nor list of elements dealt with, a brief survey of those included may be of interest to those wishing to become acquainted with the scope of this book. It includes the following elements in the order given:—Cs, Rb, Li; Be, Y, and Y earths; Ce, La, Dd, Pr, Nd; Th, Zr, Ge, Ti, Nb, Ta; In, Ga, Tl, V, Mo, W, U; Te, Se; Pt, and associated metals, Au, and the new gases of the atmosphere.

The treatment of each of these is the same; history occurrence, preparation, compounds, characteristics, and experimental work on the group.

The absence of theoretical speculations is shown throughout the work. The author is quite up to date in his methods, but is it not peculiar to find radium alongside of lucium, etherion, and other elements of "unconfirmed discovery"?

A Laboratory Guide to Qualitative Analysis with the Blowpipe. By F. M. Martin. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. 12mo. Pp. iv.—47.

This little book shows how blowpipe reactions may be used to distinguish forty-three of the elements and twenty acids. Being for the use of teachers having a comprehensive knowledge of chemical facts, details which might prove tedious have been omitted, and the entire course of testing is presented in a series of tables occupying only 30 pages. Besides using the blowpipe, many tests are made by the aid of sealed and open glass tubes on a plaster tablet, and with the assistance of several reagents, notably HI, HBr, $SnCl_4$, and $Co(NO_3)_2$, as well as the more common borax, sodium carbonate, potassium nitrate, &c.

The methods are simple and easily managed, and in skilled hands must be very satisfactory. Some of the tests are very suggestive.

Teachers will do well to give this inexpensive little book a trial. There is an index.

The Praxis of Uninary Analysis. A Guide to the Chemical Analysis of Urine, with Directions for Preparing Artificial Pathological Urine for Practising the Various Tests, and an Appendix on the Analysis of Stomach Contents. By Lassar-Cohn. Authorised Translation from the Author's Enlarged and Revised Second Edition, by H. W. F. Lorenz. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1903. 12mo. Pp. 58.

The first edition of this useful little book was published in 1897, and it met with such great success that a second edition was called for within six months. This translation by Dr. Lorenz will make it available to those preferring the English language, especially students of medicine. Following the introduction, the book deals with qualitative tests, quantitative methods, the character of normal urine, and, lastly, the analysis of stomach contents. An excellent feature of the book is the presentation of methods excluding ambiguities and convenient of performance. The book can be recommended to those having limited training in chemical analysis. H. C. B.

International Catalogue of Scientific Literature. First Annual Issue. D. Chemistry, Part II. Published for the International Council by the Royal Society of London. London: Harrison and Sons. Paris: Gautier-Villars. Jena: Gustav Fischer. 1903. Pp. 671.

The "International Catalogue of Scientific Literature," commencing with the literature of the year 1901, is an outgrowth of the "Catalogue of Scientific Papers" published by the Royal Society of London. The history of its inception and the means adopted to bring the idea to a practical issue has been already given in our columns.

The branches of science to be included in the catalogue are seventeen in number, and the volume now before us is marked D, and deals with Chemistry. A Schedule of Classification and an Index thereto are prefixed to each volume in English, French, German, and Italian; this will not only enable the scientific worker to study the classification in the language with which he is the most familiar, but also in cases of doubt enable him to refer to the corresponding entry in another language. The various headings and sub-headings throughout the Subject Index are given in English; the entries in the Subject Indexes are in the language of the original paper when that is one of the five following languages:—Latin, English, French, German, and Italian, but in cases of translation the name of the original language is given in rounded brackets.

In the Authors' Catalogue each title is given in the original language, subject to the above mentioned restrictions.

After reading the instructions as to the method and marks used in cataloguing, any entry can be found without much difficulty. We think, however, that it would facilitate matters if "headlines" could be placed at the top of each page, giving some reference as to the subject dealt with on such a page. At the end of the volume there is a list of journals referred to with their abbreviated titles, a short list of errata on page 648, and an index to the subject catalogue.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 13, September 28, 1903.

Compound of Aluminium Sulphate with Sulphuric Acid.—E. Baud.—When bauxite is acted upon by sulphuric acid diluted with its own volume of water, as in the case of the preparation of aluminium sulphate, after a definite time of heating a copious crystalline deposit is formed. This is evidently not ordinary aluminium sulphate, as it is not precipitated by sulphuric acid, and also it only dissolves with difficulty in cold water. If the bauxite is replaced by pure aluminium hydrate the same phenomenon occurs. After purifying and drying, the substance is found to have the composition $Al_2O_3.4SO_3.4H_2O$. It dissolves very slowly in cold water, but more rapidly in hot. The formation of this compound is probably the result of three concurrent phenomena: partial dehydration of the aluminium sulphate, $Al_2(SO_4)_3,16H_2O$, combination with sulphuric acid, and molecular modification.

Nitrosite of Pulegone.—P. Genvresse.—The nitrosites of the cyclic ketones possessing one or several double liaisons have up to the present time never been prepared. The author experiments on carvone and pulegone. In the case of carvone the experiments were unsuccessful, but pulegone nitrosite, $C_{10}H_{16}ON_2O_3$, can be obtained by two methods—from amidon and nitric acid either with nitrogen peroxide or with nitrous vapours.

Preparation of Sulphuretted Hydrogen from Organic Extracts and Albumenoid Matter in general.—E. Pozzi-Escot.—When an extract is made of residues from a brewery by the method described in a former paper, and this extract is mixed with flowers of sulphur, a large quantity of sulphuretted hydrogen is evolved at ordinary temperatures. The same extract treated with chloroform, but not with sulphur, gives off no sulphuretted hydrogen in twelve hours at ordinary temperatures. If, however, this latter extract is boiled for three minutes, and, after cooling, chloroform and flowers of sulphur are added, no evolution of gas takes place. The aqueous extract of the residue, if brought to boiling-point in presence of sulphur, immediately gives forth a copious evolution of sulphuretted hydrogen when hot, but, on cooling, and the vessel being absolutely freed of all trace of this gas by agitation with carbon dioxide and left for twelve hours at the laboratory temperature, no further evolution of sulphuretted hydrogen can be obtained. On the other hand, if the aqueous extract is left in presence of sodium bisulphite, at the end of a definite time a considerable quantity of sulphuretted hydrogen is evolved. From these experiments and certain others, it appears reasonable to conclude that the production of sulphuretted hydrogen, in abundance and without limit, by organic extracts, and in particular by extracts of brewing residues, is due to a phenomenon of a diastasic nature.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxix., No. 8.

A New Class of Peruranates.—J. Aloy.—Already inserted in full.

Quantitative and Qualitative Analysis of Cobalt Compounds.—H. Copaux.—Already inserted in full.

Oxidation by means of Chromic Acid in the presence of other Acids.—Maurice Prud'homme.—To obtain a white design on a background of indigo the tissue is printed with a colour containing chromate of potash or soda. It is then passed through a bath heated to 50°, generally containing 50 grms. of oxalic acid and 50 grms. of sulphuric acid; the tissue is left in for half a minute or a minute. During this time, the liberated chromic acid must oxidise and destroy the indigo. Experiments made by the author with a mixture of chromic and oxalic acids have shown that:—When the chromic acid remains constant, the speed of oxidation of the indigo varies proportionally to the amount of oxalic acid. When the weights of the chromic and oxalic acids vary, but retain constant proportion one to the other, the speed of the oxidation varies according to the square of the weight of the oxalic acid; the speed of oxidation is also proportional to the product of the masses of the chromic and oxalic acids present. By using sulphuric acid instead of oxalic acid, analogous results were obtained. This fact is the more remarkable since sulphuric acid is not a reducing agent like oxalic acid, to which a certain facility of starting the oxidation by means of chromic acid has been attributed, on account of its reducing properties. The result of the research is the finding of the following general rule:—The speed of the reduction of chromic acid by oxalic acid is proportional to the weight of the chromic acid and to the number of molecules of oxalic acid, which exceeds 3, and inversely proportional to the dilution.

Action of Metals at a High Temperature on the Fatty Acids.—Alexandre Hébert.—Already noticed.

On the Mechanism of the Action of Zinc Powder at a High Temperature on the Fatty Acids.—Alexandre Hébert.—The action of zinc powder at a high temperature on the lower fatty acids gives rise to fairly simple carbides, which are related more or less directly to the original acid; but as soon as we rise in the series, and take, for instance, the C_{12}, and even to a greater extent with the C_{18} groups, there is at the same time as the reaction a more or less complex and profound polymerisation, producing ethylenic carbides of high molecular weights, and which cannot be connected, at any rate in a simple manner, with the fatty acids from which they have sprung.

Essence of Roman Camomile. Preparation of Angelic Acid. Preparation of Tiglic Acid.—E. E. Blaise.—To effect the synthesis of the $\alpha\beta$-dimethylglutaric acids, the author turned to the condensation of the angelic and tiglic ethers by means of cyanacetate of ethyl soda, but he had to prepare first the angelic and tiglic acids. As angelic acid could not be obtained synthetically, it was extracted from essence of Roman camomile by saponification; 500 grms. of the essence gave 65 grms. of re-crystallised angelic acid. To prepare tiglic acid, the author had recourse to the dehydration of α-methyl-β-oxybutyric acid; the ether corresponding to this acid was prepared by condensing ordinary aldehyde and α-bromopropionic ether in the presence of zinc. 150 grms. of α-methyl-β-oxybutyric ether were poured gradually on to 225 grms. of perchloride of phosphorus. The action was terminated by heating for half-an-hour on a water-bath, then decomposing by means of water. The raw product thus obtained contains about 33 per cent of tiglate of ethyl and 66 per cent of β-chlorised ether. It is saponified directly with alcoholic potash, which at the same time transforms the chlorised ether into tiglic acid. After the elimination of the alcohol, the acid recovered from the alkaline salt consists of almost pure tiglic acid, which crystallises rapidly. The transformation of angelic and tiglic acids into ethylic ethers is effected very easily by heating these acids on the water-bath for six hours with one and a-half times the theoretical quantity of absolute alcohol treated with 15 per cent of sulphuric acid.

Isopyromucic Acid.—G. Chavanne.—Already noticed.

A New Product of the Reduction of Dinitrostilbene-disulphonic Acid: Nitroamidostilbene-disulphonic Acid.—A. Wahl.—One hundred grms. of dinitrostilbene-sulphonate of sodium were dissolved in 1000 c.c. of warm water and cooled down to 30—40°. We then add slowly a solution of 70 grms. of crystallised sulphide of sodium in 400 c.c. of water. The addition of the sulphide causes a slight rise of temperature, which is checked by placing the flask in cold water. After about a quarter of an hour, all the soda salt of the dinitrostilbene-disulphonic acid has disappeared; acidulate with 100 c.c, of concentrated hydrochloric acid. An abundant yellow crystalline precipitate is formed, which, after complete cooling, is drained and washed with salt water. This product can be purified by dissolving it in carbonate of sodium and precipitating the filtered solution with hydrochloric acid. To obtain it perfectly pure, it is dissolved in boiling water, acidulated with acetic acid, and left to crystallise by cooling. The analysis of this product, dried at 130—150°, corresponds to the formula $C_{14}H_{11}N_2O_8S_2 - Na$; that is to say, an acid sodium salt of nitro-amido-stilbenedisulphonic acid.

Diethylorthoxyphenylcarbinol and its Derivatives.—A. Mounié.—The author has examined the products of the reaction of bromide of ethyl-magnesium on salicylate of methyl, to verify, in particular, whether the first isolable product would not be the tertiary alcohol expected,—

$$C_6H_4 \begin{cases} COH \; (1) \\ OH \end{cases} < \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \; (2).$$

He easily attained his object; the tertiary alcohol thus obtained is the diethylorthoxyphenylcarbinol, which is a perfectly stable crystalline body under ordinary conditions, but which decomposes when distilled *in vacuo*.

MISCELLANEOUS.

Conditions which Determine the Sign and the Magnitude of Electrification by Contact.—Jean Perrin.—Electric osmosis affords an easy method of investigating the charge due to contact of any solid and any liquid. The charge produced is larger in proportion as the body is capable of easy ionisation, such as water. The electrification is, in fact, due to the ions present in the liquid. The only ions which are directly active in water are H+ and OH−. Each of these takes a charge corresponding to its sign. All polyvalent positive ions diminish the action of the OH^{-1} ions present, and all polyvalent negative ions that of the H+ ions. This paralysant action increases with the concentration and with the valency.—*Comptes Rendus*, cxxxvi., No. 14.

Casting Copper in Sand.—(*Metal Industry*).—If the copper has overheated, it often explodes as it sets, and no good castings are produced. If it is cast without being overheated, liquid copper oozes from the gate for some time during setting, while the casting is full of blow-holes, caused by carbonic oxide. Phosphorus can absorb the oxygen present in the metal as cuprous oxide, but not that as carbonic oxide. Silicon can do both. One pound of silicon-copper containing 10 per cent of silicon is added to 100 pounds of copper, introducing 0·1 per cent of silicon. This amount suffices, if the copper is kept well covered with charcoal and not overheated. A plumbago stirrer is used for mixing the bath, and time is given for the silica formed to rise to the surface. The metal is then skimmed and poured. The silicon may be doubled, if high electrical conductivity of the castings is not a prime desideratum. The precautions to take are summarised as:—1. Use a clean crucible and keep it for this work. 2. Use graphite stirrers and skimmers; iron is rapidly attacked by silicon. 3. Keep metal well covered with charcoal. 4. Do not overheat. 5. Stir. and give time for silica to rise. 6. Cast pattern with finished side down, avoiding blow-holes in it, which rise to the upper surface. 7. Do not pour too cold. 8. Silicon will not make up for carelessness in handling the metal.—*Journ. Am. Chem. Soc.*, xxv., No. 5.

NOTES AND QUERIES.

**** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Nitrogen fixing Bacteria.—I should feel very much obliged if you could give me the address of a laboratory where I can obtain "Alinit," the nitrogen-fixing bacteria for applying to land to increase its fertility. I am anxious to obtain a phial of this for experimental purposes, and will feel very grateful if any of your correspondents can oblige me. Can you also give me any useful and late publications referring to atmospheric nitrogen-fixing bacteria?—HOWARD B. EVANS.

MEETINGS FOR THE WEEK.

MONDAY, Nov. 2nd.—Royal Institution, 5. General Monthly Meeting.
—— Geological, 8.
—— Society of Chemical Industry, 8. "On the Application of the X Rays to the Examination of 'Safety Fuses,'" by C. Napier Hake, Chief Inspector of Explosives, Melbourne, Australia (to be read by Prof. W. R. Hodgkinson). "Scarlet Phosphorus—A New Chemically Active Variety of Red Phosphorus, and its Use in the Manufacture of Matches," by Drs. Marquart and Schulz (to be read by W. Muir). "New Compound of Phosphorus for the Production of Ma ches" by F. Bale. "Densities of Concentrated Nitric Acid at Different Temperatures," by Prof. V. H Veley, F.R.S., and J. J. Manley. "On a Comparison of different Types of Calorimeters," by J. S. S. Brame and Wallace A. Cowan.

THURSDAY, 5th.—Chemical, 8. "Conductivity of Substances Dissolved in certain Liquefied Gases," by B. D. Steele and D. McIntosh. "The Reduction of Hydrazoic Acid," by W. T. Cooke. "The Behaviour of Metallic Oxides towards Fused Boric Anhydride," by C. H. Burgess and A. Holt, jun. "Some Reactions of Vanadium Tetrachloride," by B. D. Steele. "Studies on Comparative Cryoscopy—Part I., The Fatty Acids and their Derivatives in Phenol Solution," by P. W. Robertson. "The Vapour-pressures of Sulphuric Acid Solutions," by B. C. Burt. "The Viscosity of Liquid Mixtures," by A. E. Dunstan and W. H. C. Jemmett. "Additive Compounds of *s*-Trinitrobenzene and Alkylated Arylamines," by H. Hibbert and J. J. Sudborough. "A Contribution to the Study of the Reactions of Hydrogen Peroxide," by J. McLachlan. "The Constitution of certain Silicates," by C. Simmonds. "Constitution of Ethyl Cyanacetate, Condensation of Ethyl Cyanacetate with its Enolic Form," P. Remfry and J. F. Thorpe. "Interaction between Chloric and Hydriodic Acids," by J. McCrae. "3 : 5-Dichloro-1 : 1 : 2-trimethyldihydrobenzene" (a Correction), by A. W. Crossley. "The Estimation of Hydroxylamine," by H. O. Jones and F. W. Carpenter. "A Study of the Isomerism and Optical Activity of Quinquevalent Nitrogen Compounds," by H. O. Jones. "The Action of Water and Dilute Caustic Soda Solutions on Crystalline and Amorphous Arsenic," by W. T. Cooke. "The Union of Carbon Monoxide and Oxygen, and the Drying of Gases by Cooling," by A. F. Girvan.

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2293.

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 212).

Chapter III. (*continued*).

Evolution of Heat by the Salts of Radium.

MM. Curie and Laborde have recently discovered that *the salts of radium are the source of a spontaneous and continuous evolution of heat.* This evolution has the effect of keeping the salts of radium at a temperature higher than that of their surroundings; an excess of temperature of 1·5° has been observed. This excess of temperature is dependent upon the thermal insulation of the body. MM. Curie and Laborde have determined the amount of heat produced in the case of radium. They found that the output is of the order of magnitude of 100 calories per grm. of radium per hour. One grm.-atom (225 grm.) of radium give rise in one hour to 22,500 cal., a quantity of heat comparable to that produced by the combustion of 1 grm.-atom (1 grm.) of hydrogen. So great an evolution of heat can be explained by no ordinary chemical reaction, more particularly as the condition of the radium remains unaffected for years. The evolution of heat might be attributed to a slow transformation of the radium atom. If this were the case, we should be led to conclude that the quantities of energy generated, during the formation and transformation of the atoms, are considerable, and that they exceed all that is so far known.

Chemical Effects produced by the New Radio-active Bodies.

Colourations.—The radiations of strongly radio-active bodies are capable of causing certain chemical reactions. The rays emitted by radium products exercise colouring actions upon glass and porcelain.

The colouration of glass, generally brown or violet, is very deep; it is produced in the body of the glass, and remains after removal of the radium. All glasses become coloured after a longer or a shorter interval of time, and the presence of lead is not essential. This fact may be compared to that recently observed of the colouration of the glass of vacuum tubes, after having been long in use for the production of Röntgen rays.

M. Giesel has demonstrated that the crystallised halogen salts of the alkali metals become coloured under the influence of radium, as under the action of cathode rays. M. Giesel points out that similar colourations are obtained when the salts of the alkalis are exposed to sodium vapour.

I investigated the colouration of a collection of glasses of known composition, kindly lent me for the occasion by M. Le Chatelier. I observed no great variety in the colouration. It is generally brown, violet, yellow, or grey. It appears to be associated with the presence of the alkali metals.

With the pure crystallised alkali salts more varied and more vivid colours are obtained; the salt, originally white, becomes blue, green, yellow, brown, &c.

M. Becquerel has discovered that yellow phosphorus is transformed into the red variety by the action of radium.

Paper is changed and coloured by the action of radium. It becomes brittle, scorched, and, finally, resembles a colander perforated with holes.

Under some circumstances there is a production of ozone in the neighbourhood of very active compounds. Rays emerging from a sealed jar containing radium do not produce ozone in the air they pass through. On the contrary, a strong odour of ozone is detected when the jar is opened. In a general way, ozone is produced in the air when the latter is in direct contact with the radium. Communication by a channel, even if extremely narrow, suffices; it appears as if the production of ozone is associated with the propagation of induced radio-activity, of which we shall speak later.

Radium compounds appear to change with lapse of time, doubtless under the action of their own radiation. It was seen above that crystals of barium-radium chloride, which are colourless when formed, become gradually coloured first yellow or orange, then pink; this colouration disappears in solution. Barium-radium chloride generates oxygen compounds of chlorine; the bromide those of bromine. These slow changes generally manifest themselves some time after the preparation of the solid product, which at the same time changes in form and colour, becoming yellow or violet. The light emitted also becomes more violet.

A solution of a radium salt evolves hydrogen (Giesel).

Pure radium salts seem to undergo the same changes as those containing barium. However, crystals of the chloride, deposited in acid solution, do not become sensibly coloured after some time has elapsed, whereas crystals of barium-radium chloride, rich in radium, become deeply coloured.

Production of Thermo-luminosity.—Certain bodies, such as fluorite, become luminous when heated; they are thermo-luminescent. Their luminosity disappears after some time, but the capacity of becoming luminous afresh through heat is restored to them by the action of a spark, and also by the action of radium. Radium can thus restore to these bodies their thermo-luminescent property. Fluorite when heated undergoes a change, which is accompanied by the emission of light. If the fluorite is afterwards subjected to the action of radium, an inverse change occurs, which is also accompanied by an emission of light.

An absolutely similar phenomenon occurs when glass is exposed to radium rays. Here also, a change is produced in the glass while luminous from the effect of the radium rays; this change shows itself in the colouration which appears and gradually increases. If the glass is afterwards heated, the inverse change takes place, the colour disappears, and this phenomenon is accompanied by production of light. It appears very probable that we have here a change of a chemical nature, and the production of light is associated with this change. This phenomenon may be general. It might be that the production of fluorescence by the action of radium and the luminosity of radium compounds is of necessity associated with some chemical or physical change in the substance emitting the light.

Radiographs.—The radiographic action of the new radio-active bodies is very marked. However, the method of operating should be very different with polonium and radium. Polonium acts only at very short distances, and its action is considerably weakened by solid screens; it is practically annihilated by means of a screen of slight thickness (1 m.m. of glass). Radium acts at considerably greater distances. The radiographic action of radium rays may be observed at more than 2 m. distance in air, even when the active product is enclosed in a glass vessel. The rays acting under these conditions belong to the β- and γ-groups. Owing to the differences in transparency of different materials to the rays, radiographs of different objects may be obtained, as in the case of Röntgen rays. Metals are, as a rule, opaque, with the exception of aluminium, which is very transparent. There is no noteworthy difference of transparency between flesh and bone. The operation may be carried on at a great distance and with a source of very small dimensions; and very delicate radiographs are thus produced. The beauty of the radiograph is enhanced by deflecting to one side the β-rays, by means of a magnetic field, and utilising only the γ rays. The β-rays, in traversing the object to be radiographed, undergo a certain amount of diffusion, and thus cause a

* Thesis presented to the Faculté des Sciences de Paris.

slight fog. In suppressing them, a longer time of exposure is necessary, but better results are obtained. The radiograph of an object, such as a purse, requires one day with a radiating source composed of several centigrms. of a radium salt, enclosed in a glass vessel, and placed at a distance of 1 m. from the sensitive plate, in front of which the object is placed. If the source is at a distance of 20 c.m. from the plate, the same result is obtained in one hour. In the immediate vicinity of the source of radiation, a sensitive plate is instantaneously acted upon.

Physiological Effects.

Radium rays exert an action upon the epidermis. This has been observed by M. Walkhoff and confirmed by M. Giesel, since also by MM. Becquerel and Curie.

If a celluloid or thin indiarubber capsule containing a very active salt of radium be placed upon the skin, and be left thus for some time, a redness is produced upon the skin, either immediately or at the end of some time, which is longer in proportion as the action is weaker; this red spot appears in the place which has been exposed to the action; the local change in the skin appears and acts like a burn. In certain cases a blister is formed. If the exposure was of long duration, an ulceration is produced which is long in healing. In one experiment, M. Curie caused a relatively weak radio-active product to act upon his arm for ten hours. The redness appeared immediately, and later a wound was caused which took four months to heal. The epidermis was locally destroyed, and formed again slowly and with difficulty, leaving a very marked scar. A radium burn with half-an-hour's exposure appeared after fifteen days, formed a blister and healed in fifteen days. Another burn, caused by an exposure of only eight minutes, occasioned a red spot which appeared two months after, its effect being quite insignificant.

The action of radium upon the skin can take place across metal screens, but with weakened effect.

The action of radium upon the skin has been investigated by Dr. Daulos, at the Hospital of S. Louis, as a process of treating certain affections of the skin, similar to the treatment with the Röntgen rays or the ultra-violet rays. In this respect radium gives encouraging results; the epidermis partially destroyed by the action of the radium is renewed in a healthy condition. The action of radium is more penetrating than that of light, and its use is easier than that of light or of Röntgen rays. The study of the conditions of application is of necessity rather lengthy, because the effect of the application does not at once appear.

M. Giesel has observed the action of radium upon plant leaves. The leaves thus treated turn yellow and wither away.

M. Giesel has also discovered the action of radium rays upon the eye. If a radio-active substance be placed in the dark in the vicinity of the closed eye or of the temple, a sensation of light fills the eye. This phenomenon has been studied by MM. Himstedt and Nagel. These physicists have demonstrated that the centre of the eye is rendered fluorescent by the action of radium, and this explains the sensation of light experienced. Blind people whose retina is intact are sensitive to the action of radium, whilst those whose retina is diseased do not experience any sensation of luminosity.

Radium rays either arrest or hinder the development of colonies of microbes, but this action is not very intense.

M. Danysz has recently demonstrated the ready action of radium upon the marrow and brain. After one hour's exposure paralysis of the animals experimented upon occurred, and the latter usually died in a few days.

Influence of Temperature upon Radiation.

There is so far but little information regarding the manner of variation of the radiation of radio-active bodies with temperature. We know, however, that radiation subsists at low temperatures. M. Curie placed a glass tube containing barium-radium chloride in liquid air. The luminosity of the radio-active body persisted under these conditions. At the moment, indeed, of removing the tube from the cold bath, it appears more luminous than at the ordinary temperature. At the temperature of liquid air radium continues to cause fluorescence in the sulphates of uranium and potassium. M. Curie has verified, by electrical determinations, that the radiation, measured at a certain distance from the source, possesses the same intensity whether the radium be at the temperature of the atmosphere or of liquid air. In these experiments the radium was placed at the bottom of a tube closed at one end. The rays emerged from the tube at the open end, traversed a certain space in the air, and were received into a condenser. The action of the rays upon the air of the condenser was determined both on leaving the tube in the air and on surrounding it to a certain height with liquid air. The same result was obtained in both cases.

The radio-activity of radium persists at high temperatures. Barium-radium chloride after being fused (towards 800°) is radio-active and luminous. However, prolonged heating at a high temperature has the effect of temporarily lowering the radio-activity of the body. This decrease is very considerable; it may constitute 75 per cent of the total radiation. The decrease is less in proportion for the absorbable rays than for the penetrating rays, which are to some extent suppressed by heating. In time the radiation of the product regains the intensity and composition that it possessed before heating; this occurs after the lapse of about two months from the occasion of heating.

(To be continued).

ON THE RADIO-ACTIVE CONSTITUENT OF THE BISMUTH FROM JOACHIMSTHAL PITCHBLENDE.

III.*

By W. MARCKWALD.

I. *On Radio-tellurium.*

In earlier communications I had shown that from the hydrochloric acid solution of the radio-active bismuth chloride, as it is obtained from Joachimsthal pitchblende, the radio-active constituent can be separated from the bismuth in two ways. On immersing metallic bismuth or antimony in the solution, the active constituent, mixed with various other substances is deposited on the metal, and by tin chloride it is precipitated in a purer condition as a fine black precipitate. On account of the complete agreement of the last product with tellurium in all its properties—with the exception of radio-activity—I had provisionally called it radio-tellurium.

By using 6 kilogrms. of bismuth oxychloride, which resulted from about 2000 kilogrms. of pitchblende, I have obtained 1·5 grm. of this radio-tellurium. Further examination showed that it consists almost entirely of *ordinary* tellurium, so that the radio-active constituent certainly amounts to only fractions of 1 per cent. For the separation of the tellurium the metal was converted into the chloride, and the tellurium was precipitated from a hydrochloric acid solution of moderate strength by means of hydrazine chlorhydrate (A. Gutbier, *Berichte*, 1901, xxxiv., 2724). It is then still decidedly active, but in order to obtain almost inactive tellurium it is sufficient to repeat the precipitation once.

The filtrate contains the active substance still adulterated with bismuth, tin, and some tellurium. If some drops of a solution of tin chloride are added to the solution after it has been concentrated, on digesting on the water-bath a very small quantity of dark precipitate separates, and may be collected on the filter. Its weight amounted to 4 milligrms. I am not by any means convinced that this product is now a single substance. But in view of the great costliness of

* *Cf Berichte*, 1902, xxxv., 2285 and 4239; see also *Chemiker. Ztg.*, 1902, xxvi., 895.

the material, I have decided that for the present I must abstain from a further chemical examination until I am able to procure greater quantities.

The filtrate from the tin chloride precipitation still contains small quantities of the active substance, even if the filtration is repeated many times, conceivably in colloid solution. The following observations confirm this view :— If to one part of the filtrate some tenths of a milligrm. of tellurous acid in aqueous solution are added, the tellurium precipitation resulting from the excess of tin chloride completely brings down the active substance. If in another part of the filtrate a stick of bismuth is immersed, it becomes only feebly active after longer action ; but if some drops of bromine water are previously added in order to oxidise the tin chloride and to convert any colloidally dissolved metal into bromide, the active substance is com pletely precipitated on the metal rod, and it becomes exceedingly active. This phenomenon is of the greatest value, if it is desired to separate the active substance from a solution which contains much bismuth, but no tellurium. This will be further discussed hereafter.

The active substance is readily soluble in cold dilute nitric acid. On driving off the acid and taking up the residue with hydrochloric acid, the solution of the chloride is obtained, from which, by the immersion of metallic plates of copper, tin, antimony, &c., the active substance may be precipitated in a very finely divided state. In order to give some idea of the activity of such precipitates, it may be stated that on a copper plate of 4 sq. c.m. surface a precipitate of about $\frac{1}{10}$ m.grm. is sufficient to make the illumination of a zinc blende screen which is brought close to the plate visible to an audience of many hundred people.

If this substance is contained in pitchblende in much smaller quantities than radium, its separation, on the other hand, when once a suitable method has been found, presents only trifling difficulties, because chemical reactions may be employed for this purpose, which is at present not the case in the separation of radium from barium.

I am indebted to the Royal Academy of Science at Berlin for the costly material which was used in this research.

II. *On Polonium.*

My last article has been followed by many publications under the above title, the purport of which I must shortly discuss. Mdme. S. Curie (*Physikal. Zeit.*, iv., 234) guards against her incidental observation, "polonium is only a species of active bismuth," being taken to mean that she had given up seeking a new element in polonium, and communicates some reactions, recently observed by her, which the polonium enriched by her fractionation method and differing from bismuth exhibits. As regards the first point, it is quite superfluous to emphasise the fact that I had not the least intention of belittling the great and lasting reputation which the Curies have earned by the discovery of the new radio-active elements, when I quoted that sentence.

The new observations of Mdme. Curie on the properties of her enriched polonium confirm the idea, already entertained by me, that this substance is by no means identical with radio-tellurium. Polonium gives on precipitation of the nitric acid solution with water precipitates which are insoluble in acids, and of a white or yellow or brown colour, a striking difference from radio-tellurium and one which is of far greater importance than the inconstancy of the radiating power of polonium. Whether the Curies' polonium does not perhaps also contain some of the radio-tellurium is a question the examination of which must be left to the discoverers of polonium.

Two articles on this subject by F. Giesel have recently appeared. The first (*Berichte*, 1903, xxxvi., 728) essentially confirms my earlier observations, as far as they relate to the production of a radio-active precipitate on a little stick of bismuth.

In a footnote the author alludes to the fact that platinum, gold, and palladium also become radio-active to a lesser degree on immersion in the polonium solution, but leaves it an open question whether the reactions which occur are analogous to those which take place in the case of bismuth. That this phenomenon, already observed by me in the case of platinum, which, moreover, is also exhibited by tellurium, is due to quite other causes, follows from the fact that all these metals after remaining for a longer time in contact with the solution do not appreciably diminish the activity of the dissolved substance, while bismuth entirely separates the substance which carries the activity from the solution.

Giesel has not been able to prove the presence of tellurium in the polonium, and did not get the tin chloride reaction. This want of success depends only on the lack of tellurium. I have obtained "polonium" from the Chininfabrik Braunschweig, which Giesel manages. A grm. of the oxychloride was dissolved in hydrochloric acid, and a drop of tin chloride solution added. Even after lengthy digestion no visible precipitate appeared, but when the solution was filtered a preceptible brown colouration could be seen on the filter. After washing, the filter was radio-active to the highest degree, and was quite equivalent to my strongest preparation. The filter smelt strongly of ozone, and was completely destroyed in the course of some weeks. As described above, a trace of tellurous acid was added to the filtrate in order to bring down the rest of the radio-active substance. The bismuth now separated from the solution showed only feeble α-radiation, but the β-radiation was not much diminished.

In his article "On Polonium and the Inducing Character of Radium" (*Berichte*, 1903, xxxvi., 2368), which has just appeared, Giesel communicates an observation which seems to him to be capable of putting a new aspect on the polonium question. By immersing a little piece of bismuth in radium bromide solution he obtained strongly α-radiating metal ; owing to the fact that Giesel associated this observation with mine, the impression was produced that the activity might have the same cause in both cases. However, this is by no means the case.

The experiment described by Giesel was planned by me some time ago. I certainly did not possess nearly such strong radium preparations as Giesel. But even using a preparation containing about 1 per cent of radium, a little rod of bismuth immersed in it assumes strong activity. The strength of the radiation is, to be sure, not to be compared with that of my strongest radio-tellurium. This phenomenon is clearly completely analogous to the above described which Giesel and I have observed when the noble metals are immersed in polonium solutions. In both cases the active constituent was not appreciably, much less completely, withdrawn from the solution.

However, Giesel's newest communication led me to arrange another experiment, which was quickly carried out, and tended to confirm my views of the matter. 0·01 grm. of radium chloride (of about 2·5 per cent) was mixed with 0·2 m.grm. of tellurous acid in weak hydrochloric acid solution and the tellurium precipitated with tin chloride. As was to be expected the tellurium precipitated was strongly active. But in spite of the most thorough washing all precipitates from a solution containing radium are more or less active. But when the metal was dissolved off the filter with nitric acid, converted into the chloride, and precipitated from a very dilute solution on copper, the activity was scarcely capable of detection by the electroscope. Thus the tellurium rendered active by induction (?) behaves quite differently from the radio-tellurium.

Finally, I must shortly discuss a sentence in Giesel's article in order that it may not be thought that I agree with it. Giesel writes :—

"Marckwald considers that the precipitate formed on the bismuth consists, at any rate in part, of metallic polonium, and regards the electrolytic separation as the proof of the existence of an (electro-negative) element, differing from bismuth, and allied to tellurium."

In an earlier article I have emphasised to Giesel the fact that I do not lay claim to the name polonium for the radio-active substance separated by me. The idea called forth by this name is so indefinite, from the fact that it was used

when radio-active bismuth was discovered, that it is now necessary to distinguish between the Curies' and Giesel's polonium. It would be a mistake to call a third substance polonium. Hence for the present I have called the substance separated by me "radio-tellurium." By this I do not wish it to be understood that I regard its close connection with tellurium as *proved*. On all occasions I have emphasised the fact that this connection was only *conjectured* by me. This conjecture has been of much use to me, because it has suggested to me the method for the separation of the active substance; for its separation not only from bismuth, but also from tellurium. However, I am far from wishing to draw from this fact any decisive conclusions about the nature of a substance which I believe has not yet been obtained in a pure state.—*Berichte der Deutsch. Chem. Gesell.*, 1903, xxxvi., 2662).

ON RADIO-ACTIVE THORIUM.

By K. A. HOFMANN and F. ZERBAN.

We have already alluded to the fact that freshly-made thorium preparations are strongly radio-active to different degrees, according to the amount of uranium contained in the minerals (*Berichte*, 1902, xxxv., 531). More recent experiments have confirmed this conclusion, as shown in the accompanying table.

It may here be noted that the preparations marked "very feebly active" produced a decided effect on the photographic plate through black paper only after an exposure of twenty hours, while the "feebly active" almost equalled uranic-uranous oxide in photographic and ionising effect. The effect of the "very strongly active" was nine to ten times greater, and this activity could be made still greater by various methods. But after one and a-half to two years all these preparations exhibited nearly uniformly only very slight penetrating β-activity, while the ionising α-radiation fell to very nearly the value of that of the uranium preparations, and after that could hardly be further diminished. This residual activity cannot be removed even by ignition for one hundred hours (as a gas-mantle, for example), nor even by the enormous heat of reduction with magnesium in a current of hydrogen, as our latest experiments have shown. Also, on mixing the chloride with fifty times its quantity of barium chloride in solution and precipitating the barium with sulphuric acid (after standing for eight days), the activity could not be completely removed from the thorium earth from euxenite.

It might be supposed that this residual effect was due to a trace of actinium (*cf.* below); but the thorium preparations made artifically active by uranium behaved so like those obtained from the uranium minerals as regards the passing away of the activity (Hofmann and Zerban, *Berichte*, 1902, xxxv., 533) that it must at least be concluded that the original strength of the thorium activity depends upon induction by means of the uranium present in most thorium minerals.

The question whether pure thorium and its compounds possess in themselves primary radio-activity may be answered in the negative, as inactive thorium earth was obtained from orthite from Fredenstrandsrand (which was quite free from uranium)*, yttrotitanite and gadolinite (Sotersdalen in Norway). In order to show that these were undoubtedly thorium earths, 4 kilogrms. of gadolinite from Sotersdalen were prepared in the usual way, and the oxalate precipitate extracted with ammonium oxalate (*cf.* Jannasch, "Leitfaden der Gewichtsanalyse). The thorium oxalate separated from the filtrate by acidulating was ignited, and the earth repeatedly precipitated with hydrogen peroxide, and with sodium thiosulphate to ensure perfect purification.

* In minerals containing phosphoric acid the proof of the presence of uranium is best established by Laube's method (*Zeit f. Angew. Chem.*, 1889, 475.

0·0776 grm. of the sulphate of constant weight at 360° gave, after strong ignition, 0·0482 grm. of oxide, which corresponds to an equivalent weight of 57·21 (H = 1) or 57·63 (O 16), while for pure thorium the accepted values are 57·7 (H = 1) or 58·1 (O = 16).

We found that the specific gravity of the oxide was 9·112 at 20°; according to Chydenius and Damour the specific gravity of the pure thorium earth varies from 9·21 to 9·366.

Thus the results we obtained agree sufficiently with those established by other investigators to prove that the oxide isolated by us, though only in small quantities, from gadolinite (Sotersdalen) was identical with thorium earth.

It was quite without effect on the photographic plate after an exposure of twenty-four hours through thin black paper, and did not appreciably accelerate, even with varying arrangement, the discharge of a very sensitive Elster-Geitel electroscope. Generally speaking, if even a trace of activity was present, its amount would have to be estimated at 1/7th of the strength of an Auer-mantle prepared from monazite sand, and ignited for about 100 hours, as accurate experiments showed.

It was interesting to notice that the gadolinite from which this inactive thorium earth was derived exhibited the property of suddenly glowing throughout the whole mass on heating, and in greater quantities with such violence that a part of the powder was scattered like dust. No gases were evolved, but only water vapour.

2·286 grms. of gadolinite gave 0·0090 grm. of water (weighed in a calcium chloride tube), with a loss of weight of 0·0088 grm. Thus, calculated to 100 parts of the mineral, the loss of water is 0·394 per cent. Of this, 0·309 per cent of water escapes below, and 0·085 per cent of water escapes at the temperature of glowing, which was found to be about 430°. As the greater part of the water evaporates below this temperature the illumination occurring with development of heat depends, not on the dehydrating of the mineral, but on an exothermic change.

That this pyroluminescence of gadolinite from Sotersdalen is not connected with the radio-activity follows from the fact that neither the mineral itself nor its constituents, especially the thorium earth, had any effect whatever on the photographic plate or the electroscope.

While the thorium earth from the minerals mentioned above by induction with uranium is given an only temporary activity, which is sometimes considerable, the small quantities of a substance similar to thorium obtained from pitchblende, Debierne's actinium (*Comptes Rendus*, 1900, cxxix., 593, and cxxx., 906) remain very strongly active for a year. We proceeded to the treatment of the soda precipitates, to be obtained commercially, of the uranium nitrate mother-liquor, and heated the part belonging to the ammonium sulphide group as chloride with excess of sodium thiosulphate. The precipitate was extracted with hot dilute sulphuric acid, the residue ignited, and fused with potassium carbonate. The part thus obtained, which was insoluble in water and in hydrochloric acid, was evaporated with sulphuric acid, dissolved in ice-water, and the nearly neutral filtrate was precipitated with oxalic acid. The earth obtained from the oxalate was yellowish-white, and approximately showed the reactions of the thorium earth, *i.e.*, it was precipitated by thiosulphate when heated and by hydrogen peroxide, and also by oxalic acid from feebly acid solution. Also on treating the oxalate with warm ammonium oxalate solution it dissolved like thorium, but unlike the latter could not be precipitated from the filtrate either by ammonia nor by acids, but remained behind after evaporation and ignition of the dissolved portion. The solubility of the dry sulphate in ice-water, which was small in comparison with that of thorium, was noteworthy, and also the rapidity with which the ignited oxide dissolved in concentrated sulphuric acid.

This "actinium" (in Debierne's sense) differs from Giesel's emanation substance (*Berichte*, 1903, xxxvi., 344) in that it may be precipitated by means of thiosulphate, and is soluble in ammonium oxalate.

Mineral.	Amount of U_3O_8 contained in it.	Amount of ThO_2 contained in it.	Activity of the thorium earth immediately after precipitation.
Bröggerite	About 78 per cent (*a*)	About 15 per cent (*a*)	Very strongly active.
Cleveite	70 per cent on an average (*b*)	7 per cent on an average (*b*)	Very strongly active.
Euxenite	5—12 per cent (*c*)	Very small	Strongly active.
Samarskite	4—17 per cent (*d*)	About 4 per cent (*d*)	Strongly active.
Fergusonite	1·5—7 per cent (*e*)	1—3 per cent (*e*)	Feebly active.
Xenotime	0·5—3½ per cent (*f*)	0·5—3·5 per cent (*f*)	Feebly active.
Thorite	About 10 per cent (*g*)	About 50 per cent (*g*)	Feebly active.
Orangite	About 1 per cent (*g*)	About 72 per cent (*g*)	Very feebly active.
Æschynite	0·31 per cent (*h*)	About 16 per cent (*h*)	Very feebly active.
Monazite sand	About 0·1 per cent (*i*)	1—2·5 per cent (*j*)	Very feebly active.

(*a*) K. A. Hofmann and W. Heidepriem, *Berichte*, 1901, xxxiv., 914.
(*b*) Rammelsberg, "Handbuch der Mineralchemie," 2 Suppl., 2nd edition, p. 67.
(*c*) Herzfeld and Korn, "Chemie d. Selt. Erden," p. 10.
(*d*) Rammelsberg, *loc. cit.*, p. 167.
(*e*) *Ibid.*, p. 166.
(*f*) *Ibid.*, p. 138.
(*g*) Herzfeld and Korn, *loc. cit.*, p. 28.
(*h*) *Ibid.*, p. 39.
(*i*) *Ibid.*, p. 40.
(*j*) *Ibid.*, p. 37.

The ionising radiation of the purest preparations was 1500 times greater than that of uranic-uranous oxide, while the action penetrating 4 c.m. of air and aluminium foil ⅓ m.m. thick is only ten times greater than that of uranium. The phosphorescence produced on Sidot's blende was clearly visible, but the emanation was only small, and was shown by the electroscope only for about two minutes after the removal of the preparation.

Since the examination of actinium by spectrum analysis has as yet provided no certain proof of the existence of an element differing from thorium, an equivalent weight determination was carried out, using a preparation which had been purified by precipitation with ammonia, oxalic acid, and, finally, with hydrogen peroxide. 0·0306 grm. of sulphate of constant weight at 360° gave 0·0196 grm. of oxide. This corresponds to an equivalent weight of 62·87 (H = 1) or 63·32 (O = 16), while for pure thorium the values are 57·7 (H = 1) or 58·1 (O = 16).

In spite of this difference, and of the quantitative peculiarities mentioned above, it is still doubtful whether the elementary nature of actinium is really different from that of thorium, for it is possible that by very strong induction of radio-activity the chemical properties of an elementary atom may be modified. To what extent this is possible shall next be thoroughly examined.

The circumstance that the activity of the actinium preparations has not diminished in a year would not in itself be a proof that the thorium earth from pitchblende contains a primarily active element (actinium), for Hofmann and and Wölfl's (*Berichte*, 1903, xxxvi., 1040) pieces of silver and palladium made active by radio-lead chloride solution have retained their ionising power up to the present (for six months). But the fact that the activity of the thorium earth from bröggerite, clevite, euxenite, and samarskite, as well as of that made active by uranium diminished very decidedly in some months, while the small quantities of a substance similar to thorium from pitchblende did not diminish in strength in a year, argues in favour of the assumption of a primarily active actinium.—*Berichte der Deutsch. Chem. Gesell.*, 1903, xxxvi., 3093.

THE ACTION OF OXIDES OF NITROGEN ON OXIMIDO COMPOUNDS.*

By W. SLOAN MILLS, M.A., Queen's College, Galway, 1851 Exhibition Scholar.

In connection with the study of the chemistry of india-rubber, in which Professor Harries, of the University of Berlin, is at present engaged, and which takes the form in the first place of an investigation into its behaviour towards oxides of nitrogen, I was entrusted with the simpler preparatory problem to investigate the action of oxides of nitrogen on oximido compounds. For this purpose benzalisonitrosoacetone was prepared, which, on being treated with free hydroxylamine under certain conditions in methyl alcohol solution, yielded long colourless prism-shaped crystals of benzalisonitrosoacetoxime,—

$$C_6H_5CH=CH.C=NOH.CH=NOH,$$

melting at 201—202° C. These were sparingly soluble in alcohol, chloroform, and acetone, soluble in glacial acetic acid, and insoluble in absolute ether. When the oxime was suspended in absolute ether, and treated at a low temperature with nitrogen peroxide, a light flocculent precipitate of nitrate benzalmethylglyoximehyperoxide,—

$$\begin{array}{l} C_6H_6CH\,.\,CH_2\,.\,C\,.\,CH \\ \quad\quad\quad\

Isonitrosoacetone semicarbazone,—

$$CH_3.C(=N.NH.CO.NH_2).CH=NOH,$$

was prepared, and gave white crystals melting at 219—220° C. It gave Liebermann's nitroso-reaction, and was insoluble in concentrated sodium hydroxide and soluble in dilute sodium hydroxide. When heated on a water-bath with acetic anhydride acetylisonitrosoacetone semicarbazone was obtained, which, when re-crystallised from glacial acetic acid, gave cubical crystals melting at 186° C. It dissolved in dilute sodium hydroxide, and when re-precipitated with dilute sulphuric acid, needle-shaped crystals melting at 218—219° C. separated. Hence it was re-converted into the original semicarbazone by the splitting off of the acetyl group. When isonitrosoacetone semicarbazone was treated with nitrogen peroxide at a low temperature, the pseudonitrole of isonitrosoacetone semicarbazone, $CH_3C(=N.NH.CO.NH_2).CH=NO.NO_2$, was formed. It melted at 163—164° C. with sudden decomposition, and gave Liebermann's nitroso-reaction. It was soluble in dilute sodium hydroxide, giving a yellow solution which was decomposed by dilute sulphuric acid with evolution of nitrogen and oxides of nitrogen.

When isonitrosoacetone, $CH_3CO.CH=NOH$, in absolute ether solution was acted on by nitrogen peroxide at a low temperature, and the residue left on evaporation of the ether heated with benzene, red fumes were evolved and diacetylglyoxime hyperoxide,—

$$\begin{array}{l} CH_3.CO.C=NO \\ \quad\quad\quad\quad | \quad\quad | \\ CH_3CO.C=NO \end{array},$$

was produced as a yellow oil. On treating this with phenylhydrazine, the monohydrazone,—

$$\begin{array}{l} CH_3.C=N.NHC_6H_5.C=NO \\ \quad\quad\quad\quad\quad\quad\quad\quad | \quad\quad | \\ \quad\quad\quad\quad\quad\quad\quad CH_3.CO.C=NO \end{array},$$

was obtained in the form of yellow rhombic plates melting at 161—162° C. When the monohydrazone was heated with phenylhydrazine, or when the oil was treated with excess of phenylhydrazine, pale yellow rhombic plates of the dihydrazone,—

$$\begin{array}{l} CH_3.C=N.NH.C_6H_5.C=NO \\ \quad\quad\quad\quad\quad\quad\quad\quad | \quad\quad | \\ CH_3C=N.NH.C_6H_5.C=NO \end{array},$$

were formed which melted at 176° C.

FURTHER INVESTIGATION ON THE DETECTION AND APPROXIMATE ESTIMATION OF MINUTE QUANTITIES OF ARSENIC IN MALT, BEER, AND FOOD STUFFS.*

By WILLIAM THOMSON, F.R.S.E., F.I.C.

Since my paper on this subject, read before the Manchester Section of the Society of Chemical Industry on May 2nd, 1902, and published in the *British Food Journal*, 1902, vol. iv., Nos. 44 and 45, and in the *Medical Chronicle* for October, 1902 (also in Chem. News, vol. lxxxvi., p. 179), I have continued the investigation with the view of improving on the process there described for detecting and estimating minute quantities of arsenic.

Wrapping the Heated Portion of the Tube in Copper Wire Gauze.

It was recommended by the Joint Committee of the Society of Chemical Industry and of the Society of Public Analysts, that a piece of copper wire gauze about one inch square be wrapped round the tube which receives the mirror at the point at which it is heated (immediately before the drawn-out portion). I directed my attention to find what advantage this offered over the heating of the naked glass tube, and ascertained that the use of the copper wire gauze was a positive disadvantage, the mirrors being less distinct with, than without, the wire gauze. Fig. 2 (*a*) shows photographic production of the mirrors in three tubes, which were obtained from 50 c.c. of a solution containing $\frac{1}{50\,0\,0}$ of a grain per gallon of arsenic trioxide, As_4O_6, in which the naked tube was heated, whilst Fig. 2 (*b*) shows photographic productions of mirrors in three tubes in the production of each of which 50 c.c. of the same solution were used, but where the heated portion of the tube was wrapped in one layer of copper wire gauze, as recommended by the Joint Committee. It will be seen on comparing these two series of tubes, that in each case more distinct and reliable mirrors are obtained by heating the naked tube than by heating it when wrapped in wire gaze.

I tried to determine the temperature at which small quantities of arsenic would be deposited from arseniuretted hydrogen, mixed with free hydrogen by placing the tube for receiving the mirror at right angles through an iron tube, underneath which was a Bunsen flame which was

* From the *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, xlvii., Part 6.

Fig. 1.

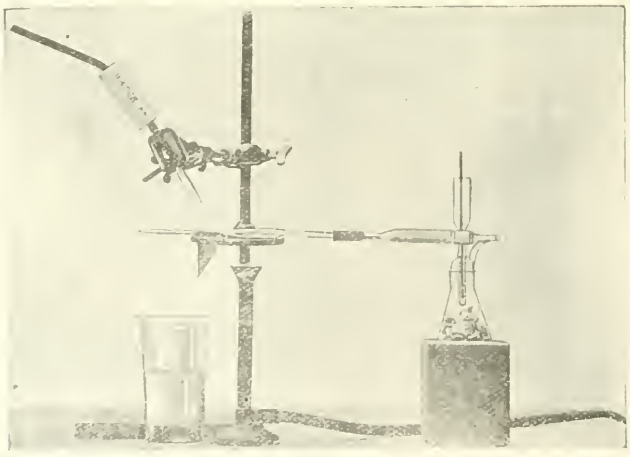
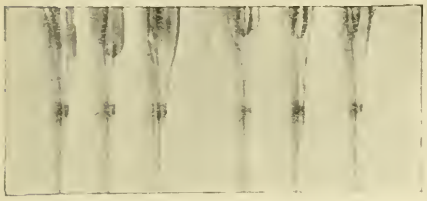


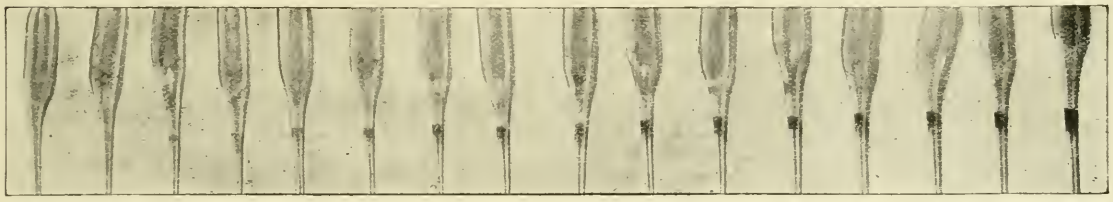
Fig. 2.



(*a*). (*b*).

Fig. 3.

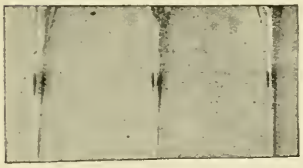
Fig. 4.



Free Acid & Zinc. 1/2000 1/1000 1/666 1/500 1/333 1/250 1/200 1/166 1/143 1/125 1/111 1/100 1/88 1/66
(Grains per gallon).

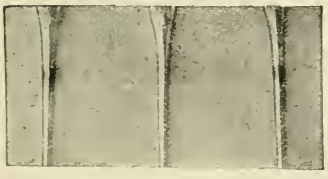
Figs. 5 and 6.

Hydrogen.



Figs. 7 and 8.

Open. Air. Hydrogen. Nitrogen. Carbon dioxide.
1 2 3 4 5 6 7 8 9 10



gradually raised, but I found that when heated to the full safety range of my thermometer, viz., 393° C., no trace of arsenic mirror was produced on the cooled part of the drawn-out portion of the tube. This result does not confirm the statement made in D. Mendeléeff's "The Principles of Chemistry" (English edition, 1897), vol. ii., p. 182, where he says, in speaking of arseniuretted hydrogen:—"But its presence in the most minute quantities may be easily recognised from the fact that it is *easily decomposed* by heat (200° C. according to Brunn) into metallic arsenic and hydrogen."

The gas containing arseniuretted hydrogen requires to be heated to a very high temperature before all the arsenic is deposited as a mirror, and it appears evident that the wire gauze prevents the attainment of the necessary temperature for the complete decomposition of all the arseniuretted hydrogen present.

Influence of Temperature at the Drawn-out Portion of the Tube on which the Mirror is Deposited.

With the view of obtaining information as to this, I used for each of the following tests 50 c.c. of a solution containing $\frac{1}{10}$ of a grain of arsenic trioxide per gallon.

The tubes used are rather wider at the drawn-out parts

than those which I now prefer to use, the first mirrors forming at a point having an internal diameter of about 0·063 of an inch (1·6 m.m.).

Tube No. 1, Fig. 3, shows the photographic representation of the mirror obtained in the ordinary way, by heating the naked tube with the top of a Bunsen flame 4 inches long, protected from draughts by a conical chimney to within an inch of the top of a flame, as previously described by me. It will be observed that two deposits have formed near to each other. The first has a brownish metallic appearance, and the second is black.

The result of the second experiment is shown in tube No. 2 in this series. This tube was enclosed in another tube between the points (*a*) and (*b*), kept at 100° C. by passing a current of steam through it, and half-an-inch from the end of the steam jacket the tube was cooled by means of a piece of tissue paper over which a current of cold water was kept rapidly dropping.

It is remarkable that the temperature of boiling water prevented the formation of the mirror altogether. The small ring of mirror formed just outside the beginning of the steam jacket, whilst the uncondensed arsenic passed for half-an-inch along the tube outside the steam jacket without depositing, and only made its appearance as a black deposit at the point (*c*) where it came in contact with the cooling effect of the stream of cold water.

The outside of the tube No. 3 in the series was covered with one layer of tissue paper from (*d*) to (*e*), and a stream of water at 50° C. was kept flowing over it. It is remarkable that at this temperature the bulk of the arsenic was deposited at the point where the comparatively hot water flowed over the tube, and it is curious to observe that on the further portion of the tube heated to this temperature no further mirror formed, but when the gas passed along the tube to the part which was not heated (to 50° C.) a second faint black deposit was formed, and, after leaving an interval of the tube free from deposit, a third, still fainter, black deposit made its appearance.

The tube No. 4 in this series was cooled by placing over it between the points (*f*) and (*g*) a single layer of tissue paper, which was cut into a triangular shape at the bottom, and over which water at 15° C. was kept rapidly dropping, as shown in Fig. 1. In this tube only one mirror was formed at the point where it came in contact with the cooled tube.

It was evident, then, first, that the cooling of the tube was an important condition for obtaining the largest mirrors; secondly, that when the tube was cooled to about 15° C. only one mirror formed; thirdly, that that mirror had a metallic lustre, and no second or third black deposit ever formed on any other part of the tube.

Since making these experiments I find that two other chemists have drawn attention to the importance of cooling the portion of the tube arranged for receiving the mirror, the first being Gabriel Bertrand, who employs a strip of filter-paper 4 to 5 m.m. wide wrapped two or three times round the tube, and fed with water drop by drop; and the second A. Gautier (*Bull. Soc. Chim.*, 1902, p. 27; 20, 21), whose method consists in applying a brass rider, the lower part of which is kept immersed in crushed ice.

My experience has shown that the best results have been given by a piece of tissue paper 3 or 4 inches long by ⅜-inch wide, folded in the centre, and hung over the tube for receiving the mirror, over which water is allowed to drop rapidly, the two hanging folds being cut to a point to allow the water to run off in a single stream into a glass placed underneath. A roll of several layers of filter-paper is not so effective for cooling, as the cold water takes some time to penetrate the several layers of paper.

Brown-metallic looking Mirrors and Black Arsenic Deposits.

It has been suggested by the Joint Committee above mentioned, and by other chemists, that the presence of oxygen or air, if mixed with the hydrogen from the generating apparatus, tends to produce black deposits rather than metallic arsenic mirrors; this seems to be so, but the explanation appears to be that the heat produced by the burning of the oxygen and hydrogen at the red-hot portion of the tube, evaporates the mirror after it has been deposited in the brown-metallic condition, and it then deposits a little further on in the black form. On gently warming the brown-metallic mirror with a small Bunsen flame, whilst the hydrogen is still flowing, the metallic mirror is evaporated and deposited a little further on as a black deposit. I have tried thus converting the metallic mirrors into black deposits, with a view to ascertain whether such deposit would form a better measure of the quantity of arsenic present than the metallic mirror, but have found that the quantities are better indicated by the brown-metallic mirrors than by the black deposit.

I have studied somewhat more minutely these two forms of arsenic. The first, or brown form, with metallic lustre, is that which is crystalline and firmly adherent to the glass tube; the second, or black form, is amorphous, and can easily be removed from the tube by gentle rubbing.

I was led to believe that the amorphous form contained occluded gaseous matter, and I have spent some time in collecting a quantity of it (several grms.), which was placed in a tube from which the air was exhausted by a Töpler pump, which is the method employed by Sir William Ramsay for removing helium from various minerals. After the tube was exhausted till no further gas could be drawn from it, the black arsenic was heated, and it volatilised and condensed in the crystalline form, but no trace of gaseous matter was liberated from it.

Internal Diameter of the Tube upon which the Arsenic Mirror is Deposited.

As the tubes used by me are all drawn out in the same manner from previously selected tube, they are found to be very closely the same in the internal diameter of the bore, but, as these tubes are slightly conical, I devised a simple measuring arrangement for obtaining the mirrors on exactly the same internal diameter of tube. This consists of an iron wire with the one end thinner than the other; the thicker end is first put into the drawn-out portion of the tube and then the thinner end, to see that the difference in the distance between which they enter is about ¼ of an inch, which it generally is, although the distance of the wider portion from the beginning of the drawn-out part varies slightly; the tissue paper for cooling is then placed so that the edge nearer the flame is exactly at the point where the entrance of the thicker end of the wire is arrested, and the mirrors, being all deposited at this point in the different tubes (where the cold water comes in contact with the glass), more accurate measures of the quantities of the deposits are obtained.

With the view of keeping the tubes hot to the point at which the cold water comes in contact with the narrow glass tube, to prevent the formation of a mirror before the portion of the tube is reached on which it should be deposited, I put a small coil of copper or platinum gauze ⅝ of an inch square around the tube, so as to cover the rounded part of the drawn-out portion and part of the narrow tube to within 1½ m.m. of the paper. I use a flat Bunsen flame *one* inch wide, the flame acting on about ¾ of an inch of the uncovered glass tube, with the end of the flame playing on the wire gauze.

Fig. 4 shows mirrors obtained by the cooling process on the tubes of accurately measured internal diameter.

The apparatus employed for carrying out the process is shown in Fig. 1.

Fading of the Arsenic Mirrors and Black Deposits.

In my previous papers on the approximate estimation of arsenic, I have mentioned that I had not observed that any of my arsenic mirrors had faded even when exposed to air and light, but, as other chemists had had experience of fading, and had recommended the sealing of the mirrors in an atmosphere of hydrogen to prevent it, I considered it desirable to carry out this process, and have since done so.

I was much surprised, however, to find that the mirrors which were made by the old process, and the original photographs of which are seen in Fig. 5, faded after exposure to the light for six weeks; a second photograph of the same, taken after exposure, is shown in Fig. 6.

It is difficult to imagine why these arsenic mirrors and deposits should have wholly or partially disappeared after being sealed up in an atmosphere of hydrogen. It is curious, however, that, whilst the mirror from the middle tube has entirely disappeared, those in the first and third tubes have only partially faded.

Other instances of fading are shown in the photographs Figs. 7 and 8, all the deposits being obtained by the old process, in which the tubes were not cooled with water. The tubes Nos. 1 and 2 were unsealed, 3 and 4 were sealed in air, 5 and 6 in hydrogen, 7 and 8 in nitrogen, and 9 and 10 in carbon dioxide, the mirrors being from the same amount of arsenic solution. The tubes 2, 4, 6, 8, and 10 were detached from the card and exposed to the light for one month, the others being kept in the dark; they were then re-mounted, and again photographed. It will be seen in Fig. 8 that the mirrors in tubes 2 and 4 (exposed to the air) and in 8 (exposed to pure nitrogen prepared by heating ammonium nitrite, and passing the same through a tube containing copper gauze heated to redness) have faded considerably, while in tubes 6 and 10 (in hydrogen and in carbon dioxide) the black or second portion of the deposit only has faded. The mirrors formed by the cooling process appeared to have suffered no change in hydrogen.

My modified and new process affords a much more accurate method of approximately estimating minute quantities of arsenic, and it is much more delicate than the process previously employed; it is, in fact, so delicate that I have now failed to get any zinc which is abolutely free from any trace of arsenic. A very distinct mirror is formed with the $\frac{1}{300}$th of a grain of arsenic trioxide per gallon, when working with 50 c.c.; that is one part in 140,000,000 parts of liquid, and half that amount can be detected; that is, one part in 280,000,000, which is equivalent to 1 grain of arsenic trioxide dissolved in 4000 gallons of beer; *i.e.*, 1 grain dissolved in 111 barrels of beer of 36 gallons each, which is equivalent to 18 tons weight of beer.

Explanation of Figures.

Fig. 1.—Apparatus employed.

Fig. 2.—Photographic production of mirrors. $\frac{1}{300}$th gr. per gallon of As_4O_6 when using 50 c.c.

(*a*) With the naked tube, heated directly with Bunsen flame.

(*b*) With the heated portion of the tube wrapped in wire gauze.

Fig. 3.—Showing the effect of temperature on the formation of the mirrors and arsenic deposits in a solution containing $\frac{1}{80}$th of a grain per gallon of As_4O_6, when using 50 c.c,

1. Ordinary Marsh test method (without special cooling.
2. Enclosed in a steam jacket from (*a*) to (*b*), and cooled with cold water at (*c*).
3. With current of water at 50° C. passing over the outside of the tube between (*d*) and (*e*).
4. With current of water at 15° C. passing over the outside of the tube between (*f*) and (*g*).

Fig. 4.—Standard bore tubes, using 50 c.c. with different quantities of As_4O_6. Cooling method.

Fig. 5.—Arsenic mirrors before exposure to the light. $\frac{1}{200}$th gr. per gallon As_4O_6 using 50 c.c.

Fig. 6.—The same mirrors seen in Fig. 5, after exposure to the light for six weeks.

Fig. 7.—Photographs of five pairs of arsenic deposits, made by the old method, respectively unsealed, and sealed in air, hydrogen, nitrogen, and carbon dioxide. $\frac{1}{100}$th gr. per gallon using 50 c.c.

Fig. 8.—Photographs of same after the right-hand one of each pair had been exposed to the light for six weeks.

THE VOLCANIC DUST OF MONT PELÉE.

By A. B. GRIFFITHS. Ph.D., &c.

Martinique is an island situated in the Caribbean Sea (14 degrees north latitude and 16 degrees west longitude), and its volcano, Mont Pelée, was extremely active last year. Mr. W. Wilson, Pharmaceutical Chemist, 281, Brixton Road, S.W., kindly sent me a specimen of the volcanic dust which he received from friends in the island. I have submitted the dust to analytical and microscopical examination, and a micro-photograph is enclosed with this note. It distinctly shows the crystalline nature of the dust. An analysis of the dust (dried at 120° C.), yielded the following result:—

Silica	55·01
Aluminium oxide	20·50
Calcium oxide	9·00
Ferric oxide	3·20
Ferrous oxide	4·86
Manganous oxide ..	0·25
Magnesium oxide ..	3·06
Potassium oxide	0·65
Sodium oxide	2·01
Titanium oxide	0·68
Sulphuric oxide	0·42
Phosphoric oxide	0·20
Chlorine	0·16
Copper, nickel, lithium	traces
	100·00

Mont Pelée dust has a specific gravity of 2·7211, and contains 3·24 per cent of magnetic material.

Mr. W. J. Townsend and others believe that the wet summer has been caused by Mont Pelée. The black steam-clouds travel in the path of the trade winds over the Gulf Stream, and "there are thousands of tons in the air still waiting to trouble us. So look out for a wet autumn and snowy winter."

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 23rd, 1903.

Dr. R. T. Glazebrook, F.R.S., President, in the Chair.

A paper on "*The Bending of Magnetometer Deflection-bars*" was read by Dr. Chree.

A theoretical paper contributed to the Society by the present author in May, 1901, proved amongst other results that the bending of the deflection-bar of an ordinary magnetometer, under the combined weight of the bar and its load, must increase the distance between the deflecting and deflected magnets, during a determination of horizontal force, to an extent which is not negligible. This conclusion has been borne out by direct observations made at the National Physical Laboratory on a number of magnetometer-bars, including specimens from the leading makers. The mean results thus obtained are recorded in the present paper. The great majority of the data were derived from direct observations made with a pair of microscopes. But a method is described whereby the necessary information can be deduced without the aid of microscopes from the magnetometer's own readings. The magnetometer is set up exactly as in an ordinary deflection experiment, with the deflecting magnet on its carriage at any convenient position on the deflection-bar, and equal weights are hung up symmetrically one on each arm. The consequent increase in distance between the two magnets diminishes slightly the deflecting force on the deflected magnet, and a slight change of

reading is observed in the magnetometer-telescope. The weights are put off and on several times, and the mean change of reading determined. As a check, it is well to observe at two distances. From the change of reading it is possible to determine the increase in distance between the two magnets. In many magnetometers the increase in distance due to the bending is roughly proportional to the distance itself. In the case of bars by the Cambridge Instrument Company the bending increased the distance by almost exactly 1 part in 10,000 at all distances. It is hoped that the method employed will prove useful to magnetic observers who have not ready access to a physical laboratory.

Prof. S. P. THOMPSON said that Dr. Chree had pointed out an important matter in magnetometry, and had told us of the existence of various sources of error. He asked why instrument makers could not design a better instrument, referring especially to the deflection-bar itself, which he said was not of a good form from an engineering point of view. Could not the bending be considerably reduced by making the bar in the form of a girder? Would it not be an advantage to lessen the weight of the carriage by making it of aluminium or of some light alloy? Prof. Thompson said that although the error referred to by the author of the paper seemed large, yet it could not be greater than errors arising from inaccuracy in the setting of the carriage or from other causes inherent in a deflection-experiment.

Dr. W. WATSON expressed his interest in the paper, and said he had never before appreciated the magnitude of the error due to the bending of the deflection-bar. In the many determinations of horizontal magnetic force which he had carried out, he had increased the effect by placing the thermometer near to the magnet on the same side of the magnetometer. He did not think it would be an advantage to lighten the carriage too much, because of the wear and tear which an ordinary magnetometer must be capable of withstanding. With regard to the accuracy of the setting of the carriage, he said that it was not easy to set it to 0·1 m.m., but that inaccuracies of setting to a certain extent compensated each other. Dr. Watson also pointed out that the position of the magnet in the carriage was not always absolutely the same.

The CHAIRMAN pointed out that the method described in the paper might be used to determine Young's modulus by bending the bar with magnets of known weight. A large number of errors entered into the determination of horizontal force, and they were being investigated one by one at the National Physical Laboratory.

Dr. CHREE, replying to Prof. Thompson's remarks, said that various attempts had been made to get rid of the bending effect. The difficulties were due to the fact that it was necessary that the bar should lie in one vertical plane, and that it should pass through the centre of the magnetometer. The error might be reduced by bending the bar so as to make the distance of the magnet from the neutral axis small, but the introduction of corners rendered the theoretical treatment of the problem difficult, and a bent bar was difficult to measure practically. In some of the magnetometers used on the United States Coast and Geodetic Survey, the deflection-bar consisted of two parts pinned together at the centre of the instrument, and although this arrangement had advantages, a great deal depended upon the pin fitting tightly. He contended that if the bending effect could be measured accurately, its magnitude was of minor importance. In the magnetometers used on the Indian Survey, the carriages were much heavier than those in use on ordinary unifilars, and the deflection-bar was constructed something like a girder. There were many causes of error in a force experiment. The formulæ used were complicated, and much depended upon an accurate knowledge of the constants P and Q.

A paper "*On the Magnetism of Basalt and the Magnetic Behaviour of Basaltic Bars when heated in Air*" was read by Dr. G. ALLAN.

Bars cut from basalt obtained from Rowley Regis and from Linz, Germany, were tested by means of a magnetometric method to determine their magnetic properties at temperatures from 15° to 800° C. Hysteresis curves are given, and the temperature-permeability curves show that whilst the English basalt has, in general, a maximum permeability near 500° C. followed by a minimum about 550° C., the temperature of maximum permeability in the case of the German basalt lay in the neighbourhood of 50 C., there being a subsequent gradual loss of strength with rise of temperature. Sections of heated and unheated rocks are given, showing evidence of chemical change in some of the rock constituents, and a table of values of susceptibility of the specimens is appended.

The CHAIRMAN expressed his interest in the paper, and said that Dr. Allen had given interesting data which would be of value in the subject of terrestrial magnetism.

Prof. W. F. BARRETT, in a letter sent to the Secretaries, said that Dr. Allan's paper was one of great interest and considerable importance, and he wished to congratulate the author on the results of his laborious investigation. Several years ago he (Prof. Barrett) examined the magnetic properties of various specimens of columnar basalt which had been taken from the Giant's Causeway in Co. Antrim, and a note on the results of this investigation was published in the *Proceedings of the Royal Dublin Society* for Dec., 1899. Each block was found permanently magnetised with a strongly marked north and south pole, the magnetic axis running diagonally through the block, and inclined to the horizon approximately at the angle of dip. As the blocks formed part of vertical columns in the Causeway, their magnetisation was undoubtedly due to the earth's magnetic field, the concave end of each block—for the ends are not plane but slightly concave or convex—was (in all the blocks examined) found to be a north-seeking pole, and must therefore have been downwards when *in situ* at the Causeway. The weight of the blocks varied from 24 to 37 kilogrms., and the specific gravity of a fragment of one of them was found to be 2·86. With such large irregular and feebly-magnetised masses only a very approximate estimate of the magnetic moment was possible by the ordinary method. This was, however, attempted, the blocks being placed on a turn-table with their centres 60 c.m. distant from the reflecting magnetometer. As might be expected, the magnet moment per grm. was found to be very small and almost alike in each side. The volume of the blocks being known, their permanent intensity of magnetisation was found to be less than that estimated by Everett for the earth, regarded as a uniformly magnetised body, viz., 0·079. Nothing could be inferred from this, as the blocks had been removed a long time from the Causeway and had been lying about in different magnetic positions to that which they originally occupied. The long retentivity of the direction of their original magnetisation in spite of rough usage was, however, somewhat remarkable.

Dr. WATSON then showed some Experiments with Electrical Oscillations.

ROYAL SOCIETY OF NEW SOUTH WALES.

General Monthly Meeting, September 2, 1903.

F. B. GUTHRIE, F.I.C., F.C.S., President, in the Chair.

"*The Separation of Iron from Nickel and Cobalt by Lead Oxide (Field's Method).*" By T. H. LABY.

The accurate separation of iron from nickel and cobalt is peculiarly difficult.

Review of Methods.

Ammonium Hydrate and Chloride.—The ferric hydrate precipitate carries down so much of the nickel and cobalt present as to require three re-precipitations.

Ammonium Carbonate.—This much-recommended separation is long and tedious.

Basic Acetate.—Using a small quantity of acetate to

precipitate the iron, 99 per cent of the nickel or cobalt can be recovered with one precipitation. But it is not readily combined with the electrolytic determination of the nickel, and sometimes the precipitate of iron is very difficult to filter. Several *electrolytic separations* have been devised; but conflicting statements have been made as to their accuracy. Gooch and Medway, using a rotating cathode, have accurately deposited nickel in half-an hour.

Rothe's extraction of ferric chloride by ether is being considerably used. The concentration of the reagents added is of more than usual importance.

Experimental.

An inquiry into the accuracy of Field's method was made, as it had distinct advantages over methods commonly in use, viz., a *single* precipitation of the iron, and the absence, after the removal of added lead, of all reagents, such as sodium or ammonium salts. Combined with the electrolytic determination of nickel or cobalt, the method becomes more rapid than, say, a double precipitation of the iron by the basic acetate process, and the precipitation of the nickel and cobalt as sulphides. Standard solutions of carefully purified iron, nickel, and cobalt nitrates were prepared. With these solutions twenty-two analyses were made, showing a recovery of over 99 per cent of nickel and cobalt, which is a somewhat better recovery than can be made by a single basic acetate separation.

"*On the Narraburra Meteorite.*" By Prof. Liversidge, M.A., LL.D., F.R.S.

Thls metallic meteorite, weighing over 70 lbs., was discovered in 1855 on the Yeo Yeo Creek, 12 miles east of Temora, New South Wales, and was exhibited to the Society by Mr. H. C. Russell, C.M.G., Government Astronomer, in 1900. A general account of the characteristics of this meteorite was given, and a series of seven slices which had been prepared so as to show the internal structure of the meteorite from the exterior to the centre. The meteorite was very difficult to cut in places. The crystalline structure is remarkable, and a series of photographs was shown to illustrate the paper.

NOTICES OF BOOKS

The Planning and Fitting-up of Chemical and Physical Laboratories. By T. H. Russell, M.A. London: B. T. Batsford. 1903.

This book will be found most useful by those who may be required to superintend the fitting-up of laboratories and science rooms, especially for educational purposes. The author shows an extensive acquaintance with the contrivances in the newest and most complete laboratories of all kinds in this country, and has described the various necessary fittings in great detail, giving many valuable hints as to the best systems to be adopted under various conditions. Careful attention is directed to the best expedients for obviating the many difficulties which arise when the accommodation for science teaching is very limited. The greater part of the book is devoted to the fitting and arranging of chemical laboratories, with many illustrations and plans and elevations, and constant references to the laboratories where the various methods have been adopted. A shorter section deals similarly with physical laboratories, and the last part contains the general principles of the ventilation, warming, and lighting of schools. In an appendix the details of the laboratory arrangements suggested by the Board of Education for secondary day and evening schools are given. Teachers of physics and chemistry, as well as architects engaged in designing laboratories and science rooms, will no doubt find in this book many useful hints and suggestions.

Treatise on Thermodynamics. By Dr. Max Planck. Translated, with the Author's sanction, by Alexander Ogg, M.A., B.Sc., Ph.D. London, New York, and Bombay: Longmans, Green, and Co. 1903.

In this translation of Prof. Planck's book on thermodynamics some necessary alterations of symbols have been made, and the author has also added a few notes, but otherwise the text of the original German edition has been closely followed. The whole subject is surveyed from a uniform point of view, free use being made of the elementary principles of the calculus, and the method of treatment may be described as that in which new laws of physics and chemistry are developed by a process of logical induction, starting from the two fundamental propositions. Thus, after an introductory chapter containing first principles and definitions, the first law is enunciated and explained, and its applications to homogeneous and non-homogeneous systems are considered. A similar process then follows with the second law and its applications to special states of equilibrium. A translation of Prof. Planck's recent paper, "Uber die Grundlage der Lösungstheorie," to which allusion is made in the translator's notice, would probably be very useful to English readers.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 14, October 5, 1903.

Conditions which Determine the Sign and the Magnitude of Electrification by Contact.—Jean Perrin.—Already noticed.

Heat of Combustion of Organic Compounds considered as Additive Properties — Alcohols and Phenols, Ether Oxides, Aldehydes and Ketones.—P. Lemoult.—In a former paper the author showed how, by the aid of five fundamental conventions, it is possible to calculate the heat of combustion of sixty carbides,—which heats have also been the object of direct measurement,—and to obtain between the two series of results a satisfactory coincidence. These conventions, the numerical basis of the calculation, are:—

$$f(\text{C—C}) = 51 \text{ cals.},$$
$$f(\text{C}_2{=}\text{C}_2) = 130 \text{ cals.},$$
$$f(\text{C}_3{\equiv}\text{C}_3) = 210 \text{ cals.},$$
$$\text{and } f(\text{C—H}) = 53 \text{ cals.}$$

$f(\text{C}_2{=}\text{C}_2)$ and $f(\text{C}_3{\equiv}\text{C}_3)$, repeated in the same molecule, losing 40 cals. The author now extends his results to all series of organic compounds.

Action of Phosphorous Acid on Mannite: Mannide.—P. Carré.—Phosphorous acid reacts on mannite to give an ether which is the result of the union of 2 molecules of acid with one molecule of alcohol. If the action of the phosphorous acid is sufficiently prolonged, the mannite is dehydrated and mannide thus produced, which enters into the reaction in its turn to give a new phosphorous ether. The phosphorous acid is etherified very rapidly by mannite, giving the ether $P_2(OH)_4O_2(CH_2)_2(CHOH)_4$. The etherification, after passing the minimum, rises very slowly and gives, finally, a phosphorous ether of mannide, $P(OH)_2O.C_6H_9O_3$. These ethers are monacids to helianthine and phthalein, in the same way as the phosphorous ethers of the other polyatomic alcohols.

Derivatives and Oxidation Products of Nitropyromucic Acid.—R. Marquis.—Nitropyromucic acid can be easily obtained by saponifying ethylic ether by water at 180°, but the employment of sealed tubes can be avoided

by effecting the saponification by means of strong boiling sulphuric acid. A mixture of 1 vol. H_2SO_4 and 1 vol. H_2O boiling at about 150° is the best strength. When the saponification is finished, the whole is diluted with water and the acid extracted from the ether. From the acid are then prepared—Methyl nitropyromucate, nitropyromucyl chloride, nitropyromucic amide, nitropyromucic anilide, and nitropyromucic-*p*-toluide. The oxidation products of nitropyromucic acid are best obtained from the ethylic ether by submitting it to the action of sodium dioxide.

Reduction of Ortho-nitrobenzyl-methylic Ether-oxide.—P. Freundler.—The author's experiments show that *o*-nitrobenzyl-methylic ether is partially saponified by alkalis, thus differing from ordinary ether oxides. This saponification may be attributed to the presence of the electro-negative group, NO_2—a fact analogous to that already noticed with regard to the phenolic ethers, which are hydrolysed little by little by boiling alcoholic potash.

MISCELLANEOUS.

Institute of Chemistry.—The Council of the Institute of Chemistry have received the Report on the Examination in Biological Chemistry, held from 20th to 23rd of October last. The Examination consisted of practical exercises in bacteriological methods as related to water supply and sewage, the microscopical examination of micro-organisms, the methods of working with and identifying vegetable enzymes, and methods for the identification and quantitative determination of the carbo-hydrates. The Candidates were also examined orally on subjects connected with their work.

Thomas Macara, A.I.C., was recommended for a Certificate in Biological Chemistry, and John Augustus Herman Brincker, B.A., M.B. (Cantab), was recommended for election to the Associateship of the Institute.

The following exercises were given :—

Tuesday, October 20th, 1903.

1. Determine the number of micro-organisms contained in the given sample of contaminated water, and also examine for the presence of *B. coli-communis*.

2. Examine the given sample of garden soil, for the presence of spore-forming anaërobic bacteria.

(NOTE.—These exercises may be continued throughout the Examination, but you must give in your note-book to-day a brief account of what you propose to do in order to complete the exercise).

Wednesday, October 21st, 1903.

Examine the given sample of fungus for the presence of the enzymes, lipase, invertase, and laccase. (Specimens of *Polyporus squamosus* and *Agaricus arvensis* were given).

(NOTE.—This exercise may be continued throughout the Examination, but you must give in your note-book to-day an account of what you propose to do).

Thursday, October 22nd, 1903.

1. The dried yeast given contains the enzyme maltase. Demonstrate its action on maltose (in the presence of toluol as an antiseptic) quantitatively by means of the polariscope. Confirm the formation of dextrose by a cupric oxide reduction determination, and by the preparation of its osazone and the determination of the melting-point of this body.

(NOTE.—This exercise may be completed to-morrow, but you must give in your note-book to-day a brief account of what you propose to do).

2. Continue the first and second day's exercises as required.

Friday, October 23rd, 1903.

1. Examine the pure cultures of the organisms supplied, and report fully on your examination. (Cultures of *Sarcina lutea*, *Schizo-saccharomyces octosporus*, a mucor, and a spore-forming bacterium were supplied). Include in your examination a measure of the dimensions of the organisms. Submit any stained or other preparations you make to the Examiner for inspection.

2. Complete as far as possible the exercises commenced on the first, second, and third days of this Examination.

MEETINGS FOR THE WEEK.

FRIDAY, 13th.—Physical, 8. (At the Royal College of Science, South Kensington). "Means for Electrifying the Atmosphere on a Large Scale" and "An Arrangement for Driving Mercury Pumps," by Sir Oliver Lodge.

BOROUGH OF SWINDON EDUCATION COMMITTEE.

SWINDON and NORTH WILTS TECHNICAL SCHOOL.

Principal—Mr. H. B KNOWLES, M.A. (Oxon.).

The Committee require the services of a LECTURER in CHEMISTRY at a salary of £150 a year.

Form of Application, which must be returned by WEDNESDAY, NOVEMBER 18th, may be had from—

W. SEATON, Secretary.

UNIVERSITY COLLEGE, BRISTOL.

The Council are prepared to appoint a PROFESSOR of CHEMISTRY in succession to Dr. Sydney Young, F.R.S., who has been elected to the Chair of Chemistry at Trinity College, Dublin.

Applications, accompanied by 24 copies of not more than four testimonials, should reach the undersigned on or before WEDNESDAY, NOVEMBER 11th. The successful candidate will be required to enter upon his duties on January 24, 1904.

Particulars as to duties, emoluments, &c., may be obtained on application.

JAMES RAFTER, Registrar and Secretary.

Office of M PHILIPPE VERZIER, Attorney in Lyons, 1, Place des Cordeliers.

SALE BY AUCTION, before the Civil Court of LYONS, on SATURDAY, NOVEMBER 21ST, 1903, at Twelve o'clock, of a MANUFACTORY recently constructed and installed, situated in Saint Fons, near Lyons, even as of the working stock, all serving to the fabrication of CHEMICALS, and enumerated in the Contract of Sale by Auction, at the upset price of 50,000 francs.

For information apply to—(1) M. PHILIPPE VERZIER, Attorney in Lyons, 1, Place des Cordeliers; (2) to M. HENRI FEYS, Trustee, in Lyons, 18, Rue du Bât d'Argent.

The Contract of Sale can be examined at the Clerk's Office of the Civil Court of Lyons, where they are deposited.

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2294.

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 224).

Chapter IV.

Communication of Radio-activity to Substances Initially Inactive.

During the course of our researches on radio-active substances M. Curie and I have observed that every substance which remains for some time in the vicinity of a radium salt becomes itself radio-active. In our first publication on this subject, we confined ourselves to proving that the radio-activity thus acquired by substances initially inactive is not due to the transference of radio-active particles to the surface of these substances. This is proved beyond dispute by all the experiments which will be here described, and by the laws according to which the radio-activity excited in naturally inactive bodies disappears when the latter are removed from the influence of radium.

We have given the name of *induced radio-activity* to the new phenomenon thus discovered.

In the same publication, we indicated the essential characteristics of induced radio-activity. We excited screens of different substances by placing them in the neighbourhood of solid radium salts, and we investigated the radio-activity of these screens by the electrical method. We observed the following facts:—

1. The activity of a screen exposed to the action of radium increases with the time of exposure, approaching to a definite limit according to an asymptotic law.

2. The activity of a screen which has been excited by the action of radium, and which is afterwards withdrawn from its action, disappears in a few days. This induced activity approaches zero as a function of the time, following an asymptotic law.

3. Other things being equal, the radio activity induced by the same radium product upon different screens is independent of the nature of the screen. Glass, paper, metals, all acquire the same degree of activity.

4. The radio-activity induced in one screen by differing radium products has a limiting value which rises with the increased activity of the product.

Shortly afterwards, Mr. Rutherford published a research, which showed that compounds of thorium are capable of producing the phenomenon of induced radio-activity. Mr. Rutherford discovered for this phenomenon the same laws as those just enunciated, besides this additional important fact, that bodies charged with negative electricity become more active than others. Mr. Rutherford also observed that air passed over thorium oxide preserves a notable conductivity for about ten minutes. Air in this condition communicates induced radio-activity to inactive substances, especially to those negatively charged. Mr. Rutherford explains his experiences by the supposition that compounds of thorium, particularly the oxide, give rise to a *radio-active emanation* capable of being carried by air currents and charged with positive electricity. This emanation would be the origin of induced radio-activity. M. Dorn has repeated, with salts of barium containing radium, the experiments of Mr. Rutherford with thorium oxide.

M. Debierne has shown that actinium causes, to a marked degree, induced activity of bodies placed in its vicinity. As in the case of thorium, there is a considerable carriage of activity by air currents.

Induced radio-activity has various aspects, and irregular results are obtained when the activity of a substance in the neighbourhood of radium is excited in free air. MM. Curie and Debierne have observed, however, that the phenomenon is quite regular when operating in a closed vessel; they therefore investigated induced activity in a closed space.

Activity induced in an Enclosed Space.

The active material is placed in a little glass jar, *a*, open at o (Fig. 11), in the centre of a closed space. Several plates, A, B, C, D, E, placed in the inclosure become radio-active after one day's exposure. The activity is the same

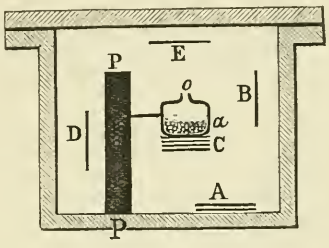

Fig. 11.

whatever be the nature of the plate, for equal dimensions (lead, copper, aluminium, glass, ebonite, wax, cardboard, paraffin). The activity of one face of one of the plates is greater in proportion to the amount of free space about this face.

If the preceding experiment be repeated with the jar, *a*, completely closed, no activity is induced.

The radiation of radium does not directly affect the production of induced radio-activity. For this reason, in the preceding experiment the plate D, screened from the radiation by a lead plate of thickness, P P, is made as active as B and E.

Radio-activity is transmitted by the air by degrees from the radiating body to the body to be excited. It can even be transmitted to a distance by very narrow capillary tubes.

Induced radio-activity is both more intense and more regular if the solid radium salt be replaced by an aqueous solution of the same.

Liquids are capable of acquiring induced radio-activity. For example, pure water may be rendered active by placing it with a solution of a radium salt within an enclosure.

Certain substanees become luminous when placed in an active enclosure (phosphorescent and fluorescent bodies, glass, paper, cotton, water, salt solutions). Phosphorescent zinc sulphide is particularly brilliant under the circumstances. The radio-activity of these luminous bodies is, however, the same as that of a piece of a metal or other body which is excited under the same conditions without becoming luminous.

Whatever be the substance made active in a closed vessel, this substance acquires an activity which increases with length of time until it attains a *limiting value*, always the same, for the same material and the same experimental arrangement.

The limit of induced radio-activity is independent of the nature and pressure of the gas inside the active enclosure (air, hydrogen, carbonic acid).

The limit of induced radio-activity for the same enclosure depends only on the quantity of radium present in the state of solution, and is apparently proportional to it.

Part played by Gases in the Phenomena of Induced Radio-activity.

Emanation.—The gases present in an enclosure containing a solid salt or a solution of a salt of radium are radio-active. This radio-activity persists when the gas is drawn off with a tube and collected in a test-tube. The sides of the test-tube become themselves radio-active, and the glass

* Thesis presented to the Faculté des Sciences de Paris

of the test-tube is luminous in the dark. The activity and luminosity of the test-tube finally completely disappear, but very gradually, and a month afterwards radio-activity may still be detected.

Since the beginning of our researches, M. Curie and I have, by heating pitchblende, extracted a strongly radio-active gas, but, as in the preceding experiment, the activity of this gas finally completely vanished.

We could discern no new ray in the spectrum of this gas; this was therefore not a case of a new radio-active gas, and we understood later that it was the phenomenon of induced radio activity.

Thus, for thorium, radium, and actinium induced radio-activity is progressively propagated through the gases, from the radiating body to the walls of the enclosure containing it, and the exciting principle is carried away with the gas itself, when the latter is extracted from the enclosure.

When the radio-activity of radium compounds is measured by the electrical method by means of the apparatus of Fig. 1, the air between the plates is itself radio-active; however, on passing a current of air between the plates, there is no observable lowering of the intensity of the current, which proves that the radio-activity distributed in the space between the plates is of little account in comparison with that of the radium itself in the solid state.

It is quite otherwise with thorium. The irregularities which I observed in determining the radio-activity of the thorium compounds arose from the fact that at this point I was working with a condenser open to the air; the least air current caused a considerable change in the intensity of the current, because the radio-activity dispersed in the space in the vicinity of the thorium is considerable as compared with the radio-activity of the substance.

This effect is still more marked in the case of actinium. A very active compound of actinium appears much less active when a current of air is passed over the substance.

The radio-active energy is therefore contained in the gas in a special form. Mr. Rutherford suggests that radio-active bodies generate an *emanation* or gaseous material which carries the radio-activity. In the opinion of M. Curie and myself, the generation of a gas by radium is a supposition which is not so far justified. We consider the emanation as radio-active energy stored up in the gas in a form hitherto unknown.

Dissipation in Free Air of the Induced Activity of Solid Bodies.

A solid body, which has been excited by radium in an enclosed space for a sufficient length of time, and which has then been removed from the enclosure, parts with its activity in free air according to an exponential law, which is the same for all bodies represented by the following formula:—

$$I = I_0\left(a e^{-\frac{t}{\theta_1}} - (a-1)e^{-\frac{t}{\theta_2}}\right).$$

I_0 being the initial intensity of the radiation at the moment of withdrawing the plate from the enclosure; I, the intensity after time, t; a is a numerical coefficient, $a = 4{\cdot}20$; θ_1 and θ_2 are time constants, $\theta_1 = 2420$ secs., $\theta_2 = 1860$ secs. After two or three hours this law becomes practically a simple exponential, and the effect of the second exponential upon the value of I is negligible. The law of dissipation is therefore such that the intensity of radiation becomes diminished to one-half its value in twenty-eight minutes. This final law may be considered as characteristic for the dissipation in an unconfined air space of the activity induced in solid bodies by radium.

Solid bodies excited by actinium lose their activity in the open air, according to an exponential law similar to the preceding, the dissipation being, however, rather slower.

Solid bodies, made active by thorium, lose their activity much more slowly; the intensity of the radiation is reduced to one-half in eleven hours.

Dissipation of Activity in a Confined Space. Velocity of Destruction of the Emanation.

An enclosure, made active by radium and then removed from its influence, loses its activity by a law which is much less rapid than that of dissipation in the open air. The experiment may be carried out with a glass tube, rendered active internally by placing it for some time in contact with a solution of a salt of radium. The tube is then sealed in the flame, and the intensity of radiation emitted by the walls of the tube is measured while the dissipation takes place.

The law of dissipation is an exponential law. It is given very accurately by the formula—

$$I = I_0 e^{-\frac{t}{\theta}}.$$

I_0 = initial intensity of radiation.
I = intensity of radiation at time, t.
θ = a time constant, $\theta = 4{\cdot}970 \times 10^5$ secs.

The intensity of the radiation is reduced to one-half in four days.

This law of dissipation is absolutely invariable whatever be the experimental conditions (dimensions of enclosure, nature of the walls, nature of the gas within the enclosure, duration of action, &c.). The law of dissipation remains the same for any temperature between $-180°$ and $+450°$. The law is therefore altogether characteristic.

In these experiments it is the radio-active energy accumulated in the gas that maintains the activity of the walls. If the gas be withdrawn and a vacuum caused in the enclosure, we have found that dissipation of activity at once occurs in the rapid method; the intensity of radiation being reduced to one-half in twenty-eight minutes. The same result is obtained when ordinary air is substituted for the active air in the enclosure.

The law of dissipation with reduction of intensity of radiation to one-half in four days, is therefore characteristic of the disappearance of radio-active energy accumulated in the gas. By making use of the expression adopted by Mr. Rutherford, the emanation from radium may be said to disappear spontaneously as a function of the time, with reduction to one-half in four days.

The emanation from thorium is of another kind, and disappears much more rapidly. The intensity of radiation diminishes to one-half in about one minute ten seconds.

The emanation from actinium disappears still more rapidly; reduction to one-half takes place in a few seconds.

Variation of Activity of Liquids rendered Active and of Radium Solutions.

Any liquid whatever becomes radio-active when placed in an active confined space. On being removed and left freely exposed to the air, the liquid rapidly loses its activity, imparting it to the gas and solid bodies surrounding it. If a liquid thus made active be placed in a closed flask, it loses its activity much more slowly; the latter being reduced in intensity to one-half in four days, just as would a gas under similar circumstances. This fact may be explained by assuming that the radio-active energy is stored in liquids in exactly the same form as in gases (in the form of an emanation).

A solution of a radium salt behaves in a somewhat similar manner. At first, it is a remarkable fact that the solution of a radium salt placed for some time in a confined space is no more active than pure water placed in a vessel in the same enclosure, when the equilibrium of activity is established. If the radium solution be removed from the enclosure and left standing in the air in a wide-necked vessel, the activity spreads itself into space, and the solution becomes nearly inactive, though still containing radium. If this solution be now enclosed in a stoppered flask, it gradually regains, in about a fortnight, a maximum of activity, which may be considerable. On the other hand a liquid made active, but not containing radium, does not regain its activity in a closed flask after having been exposed to the atmosphere.

(To be continued).

THE ATOMIC LATENT HEATS OF FUSION OF THE METALS, CONSIDERED FROM THE KINETIC STANDPOINT.

By HOLLAND CROMPTON.*

In considering the changes involved in the passage from the liquid to the solid state as a question of molecular mechanics, the simplest case is that offered by a liquid, the molecules of which are monatomic, or consist each of a single atom only. The possibility of changes occurring inside the molecule may then be regarded as excluded, and we are left with the question of the difference in the relationship of the molecules one to another in the liquid and in the solid state. There seems little reason to doubt that this difference may be regarded as primarily due to the molecules of the liquid possessing a greater freedom of motion than those of the solid. In the passage from liquid to solid it is not at all unlikely, therefore, that there is a considerable loss of molecular kinetic energy, and it is to this point that attention is directed in this paper.

According to the kinetic theory, if a gas is composed of monatomic molecules, on heating the gas the molecules acquire kinetic energy only, and if no outside work is being done this kinetic energy is approximately equivalent to 2·96 calories per degree centigrade for the grm.-molecule. In heating the gas from the absolute zero, at which the molecules would be at rest, to the temperature T, the kinetic energy acquired by the grm.-molecule is then equivalent to 2·96 T calories. Now, in the case of a liquid, although we have at present no means of ascertaining what proportion of the heat given to the liquid is used purely for the purpose of increasing the kinetic energy of the liquid molecules, it would appear probable, more especially from the comparison of the specific heats of gases and liquids, that the amount is the same for liquids as for gases. Therefore, if a liquid is heated from the absolute zero to the temperature T on the absolute scale, the heat utilised in increasing the kinetic energy of the molecules of the liquid would be 2·96 T calories for the grm.-molecule.

Taking then a liquid composed of monatomic molecules, and assuming that the passage from liquid to solid involves a considerable diminution of the kinetic energy of the liquid molecules, the energy thus removed at the temperature T should approximate to 2·96 T calories for the grm.-molecule of the liquid. If no further change takes place the latent heat of solidification of the grm -molecule should approximate then to this value. Or in other words, if A is the molecular (in this case atomic) weight, r the latent heat of solidification in the usual units, according to the above $Ar = 2{\cdot}96\ T$ or $Ar/T = 2{\cdot}96$ approximately.

It is possible to submit this result to experimental test as the latent heats of fusion of a number of the metals, presumably of monatomic molecular structure, are known.

In the following table are given the values of r, Ar, T, and Ar/T for those metals for which r has been, up to the present, determined with sufficient accuracy :—

Metal.	r.	Ar.	T.	Ar/T.
Sodium	31·8	731	370	1·98
Potassium ..	15·7	613	335	1·84
Copper	49·1	3140	1355	2·32
Silver	27·0	2920	1230	2·37
Gold	16·3	3227	1335	2·41
Zinc	28·1	1839	688	2·67
Cadmium	13·7	1531	593	2·58
Mercury	2·8	565	234	2·41
Aluminium ..	80	2166	927	2·33
Thallium	7·2	1470	562	2·61
Tin	13·3	1573	503	3·05
Lead	6·4	1340	598	2·24
Palladium	36·3	3873	1773	2·18
Platinum	27·2	5295	2053	2·58
Gallium	19·1	1336	286	4·67
Bismuth	12·5	2602	540	4·82

It will be seen that in the case of fourteen of the above sixteen metals, the values of Ar/T vary from 1·84 for potassium to 3·05 for tin, the average value being 2·4.

There is, therefore, in these cases a moderately close approximation to the predicted value of 2·96. Two metals, bismuth and gallium, give much higher values than the rest, and evidently are not in keeping with the general view here advanced. Whether this is due to these metals not possessing a monatomic structure or to some other cause cannot at present be decided.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

PREPARATION OF OXIMIDO COMPOUNDS.*

By W. SLOAN MILLS, M.A., Queen's College, Galway
(1851 Exhibition Scholar).

As it seemed desirable that the work described in the paper on "The Action of Oxides of Nitrogen on Oximido Compounds" should be extended to other oximido compounds, *m* - nitrobenzalisonitrosoacetone and cuminalisonitrosoacetone and some of their derivatives were prepared.

Molecular proportions of isonitrosoacetone and *m*-nitrobenzaldehyde were condensed to *m*-nitrobenzalisonitrosoacetone, $C_6H_4{\cdot}NO_2{\cdot}CH=CH{\cdot}CO{\cdot}CH{:}NOH$, by means of sodium hydroxide. A theoretical yield was obtained. When re-crystallised from absolute alcohol it gave slightly yellow coloured crystals, melting at 164° C., which were easily soluble in acetone, ether, and glacial acetic acid. It was soluble in dilute sodium hydroxide. When treated with phenylhydrazine a yellow crystalline hydrazone was formed melting at 99—100° C. When heated on a water-bath with excess of phenylhydrazine a dark red insoluble precipitate was obtained, which melted at 206—207° C., and proved to be the dihydrazone of *m*-nitrobenzalmethylglyoxal, $C_6H_4(NO_2){\cdot}CH=CH{\cdot}C(:N{\cdot}NH{\cdot}C_6H_5){\cdot}CH(N{\cdot}NH{\cdot}C_6H_5)$.

m-Nitrobenzalisonitrosoacetoxime,—

$$C_6H_4(NO_2){\cdot}CH=CH{\cdot}C=NOH{\cdot}CH=NOH,$$

was isolated when the ketone was treated with free hydroxylamine. It is soluble in glacial acetic acid, insoluble in absolute alcohol, and melts at 220° C. By the action of semicarbazide on the ketone *m*-nitrobenzalisonitrosoacetone semicarbazone,—

$$C_6H_4(NO_2){\cdot}CH=CH{\cdot}C(=N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH=NOH,$$

was obtained which melted at 196—197° C.

Cuminalisonitrosoacetone,—

$$(CH_3)_2{\cdot}CH{\cdot}C_6H_4{\cdot}CH=CH{\cdot}CO{\cdot}CH=NOH,$$

was prepared by the condensation of cuminol and isonitrosoacetone. It was re-crystallised from benzene, giving beautiful sulphur yellow rectangular plates melting at 162—163° C. It does not give readily a crystalline hydrazone. It is easily soluble in ether and acetone, soluble in benzene, and insoluble in petroleum ether. By the action of semicarbazid cuminalisonitrosoacetone semicarbazone,—

$$(CH_3)_2CH{\cdot}C_6H_4{\cdot}CH=CH{\cdot}C(N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH=NOH$$

was obtained, which melted at 176° C. when re-crystallised from dilute alcohol. It is easily soluble in acetone, and soluble in ethyl acetate and ether. When the ketone was treated with free hydroxylamine in methyl-alcohol solution a beautiful white crystalline oxime,—

$$(CH_3)_2CH{\cdot}C_6H_4{\cdot}CH=CH{\cdot}C=NOH{\cdot}CH=NOH,$$

was precipitated on the addition of a little water. It melted at 192° C., and was easily soluble in ether acetone and ethyl acetate, soluble in alcohol and benzene, and somewhat soluble in chloroform.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

ON THE

„SELF-INDUCTION" SPECTRA OF SILICIUM, AND ITS ASTRONOMICAL COMPARISONS.*

By Count A. de GRAMONT, Docteur ès Sciences Physiques.

MANY of the silicium lines recognised in stellar spectra have been considered characteristic of a high temperature, and I have thought it would be interesting to study their behaviour under the influence of "self-induction," and to give here that part of the spectrum susceptible of astronomical comparisons. The spectrograms show, on their upper part, the spectrum of the ordinary condensed spark of silicium, obtained with an induction coil giving a 15 c.m. spark and a condenser of 0·009 microfarad; and beneath this spectrum are photographs successively taken with "self-inductions" varying from 0·00002 Henry to 0·03000 H. The spectra were taken with two prisms of heavy flint glass, and subsequently with a calc-spar prism and quartz lenses. The silicium spectrum taken in these circumstances showed two very different categories of rays:—

1. Lines resisting a self-induction of 0·03 H., and even reinforced by it.
2. Lines commencing to grow feeble with a weak self-induction of 0·0002 H., and disappearing almost simultaneously with 0·0062 H.

Lockyer as the most remarkable of the "enhanced lines" of silicium. Under the influence of self-induction they are the last to disappear; spectrograms show that they shorten by concentrating in the vicinity of the electrodes, becoming reduced to points, and vanishing at a self-induction of 0·0062 H.

The line 3905 of the triplet ζ is very strong at the maximum self-induction employed (0·03 H.), while the neighbouring lines, 3862, 3856, scarcely visible at 0·0006 H., disappear entirely before reaching 0·0062 H.

The triplet η (3807 to 3791) appears to disappear at a still feebler self-induction.

The most refrangible part of the spectrum has no astronomical interest, for it is stopped by atmospheric absorption. I have studied it with a quartz spectrograph. The line 2542 disappears with the same amount of self-induction as above; that is to say, at less than 0·0062. All the other lines, especially the characteristic six-line group (2529 to 2507) and the group (2217 to 2208) entirely resist the maximum self-induction. Finally, I have found that the extreme line 1930·0 does not belong to silicium, but to aluminium.

These researches have been made with silicium crystallised in small octahedra and plates, then with sodium silicate fused before the blowpipe on platinum wires. As I have already shown, the effect of self-induction is the same with solid bodies as with fused salts (*Comptes Rendus*, May 5 and 26, 1902).

Permanent with "self"	α	6370	Strong.	
		6342	Strong.	
Disappearing with "self"	β	5879	Easily visible.	
		5960	Easily visible.	
Permanent with "self"	γ	5059·8	Strong.	
		5045·5	Strong.	
Disappearing with "self"	δ	4574·5	Well marked.	Seen in the very hot helium stars such as β Crucis, ϵ Canis Majoris Bellatrix.
		4567·0	Strong.	
		4552·5	Strong.	
	ϵ	4131·0	Very strong; diffused.	Found in Sirius, α Cygni, Rigel Bellatrix, ϵ Canis Majoris, Procyon, Algol, &c.
		4128·0	Very strong; diffused.	
Rather reinforced by "self"	ζ	3905·5	Very strong and sharp. Visible in the solar spectrum.	Seen in Sirius, α Cygni, Rigel, in the stars of the Groups VI. to VIII. of the Harvard College classification, where they accompany the preceding doublet, ϵ.
		3862·5	Rather strong and sharp.	
		3856·0	Strong; sharp.	
Disappearing with "self"	η	3835·0	Weak.	Seen in ϵ Canis Majoris with the groups δ and ϵ.
		3807·0	Rather strong.	
		3796·0	Rather strong.	
		3791·5	Weak.	
		3094·5	Rather strong.	
		3087·2	Rather strong.	

The doublets α and β were measured by sight only with a direct-vision spectroscope. It will be interesting to see if the group β accompanies groups δ and ϵ in the hot stars.

The triplet δ (4574 to 4552) has been recognised by M. Demarçay ("Spectres Electriques," Gauthier-Villars, Paris, 1895) as belonging to silicium in hydrofluoric solution, and by myself with free silicium and in fused silicates ("Spectres des Métalloïds dans les Sels Fondus: Silicium," *Comptes Rendus*, January 25, 1897). Notwithstanding this, these same lines, recognised by many observers in the spectra of the stars, were not attributed to silicium until 1900, when Mr. Joseph Lunt in his turn showed their origin (*Roy. Soc. Proc.*, lxvi., 44).

The doublet ϵ (4131, 4128) is considered by Sir Norman Lockyer as the most remarkable of the "enhanced lines" of silicium. Under the influence of self-induction they are the last to disappear; spectrograms show that they shorten by concentrating in the vicinity of the electrodes, becoming reduced to points, and vanishing at a self-induction of 0·0062 H.

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These researches have been made with silicium crystallised in small octahedra and plates, then with sodium silicate fused before the blowpipe on platinum wires. As I have already shown, the effect of self-induction is the same with solid bodies as with fused salts (*Comptes Rendus*, May 5 and 26, 1902).

The wave-lengths have been measured for comparison with the lines of a cadmium-lead alloy, photographed on each of the spectrograms.

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

Royal Institution.—The Annual Course of Christmas Lectures at the Royal Institution, specially adapted to young people, will be delivered by Professor Ray Lankester, M.A., LL.D., F.R.S., Director of the Natural History Department of the British Museum, whose subject is "Extinct Animals." The first lecture will take place on Tuesday, December 29, at 3 o'clock, and the remaining lectures will be delivered on December 31, 1903, and January 2, 5, 7, and 9, 1904.

THE VOLUMETRIC DETERMINATION OF MERCURY AND OF HYDROCYANIC ACID.

By LAUNCELOT W. ANDREWS.

It is a familiar fact that hydrocyanic acid is a "pseudo-acid" which possesses no acid reaction at all toward many indicators, as methyl orange, nitrophenol, &c., and which cannot be acidimetrically titrated even with the aid of extremely acid-sensitive indicators, such as phenolphthalein or toluylene red. If silver nitrate is added to a solution of hydrocyanic acid a quantitative precipitation of silver cyanide occurs, and if the silver salt is in excess, an amount of nitric acid is set free equivalent to the hydrocyanic acid used. Titration of the nitric acid by the acid of any suitable indicator, such as paranitrophenol, leads to a knowledge of the amount of hydrocyanic acid originally present. The process is accurate but not especially convenient. The precipitated silver cyanide may retain free hydrocyanic acid or silver nitrate, or both, according to the conditions of the precipitation, semipermeable "cells" being formed which give up their contents very slowly by long-continued washing, and which continue to exhibit an acid reaction even after washing with excessive amounts of water. This difficulty can be brought within bounds by precipitating from highly dilute solutions. It might be thought possible to titrate the free nitric acid directly, without filtering from the precipitate, and such is in fact the best mode of proceeding. Nitrophenol is a good indicator for the purpose, although methyl orange may be used. Lacmoid forms an insoluble compound (silver salt ?) which disturbs the sharpness of the end-reaction. If the hydrocyanic acid is in excess, and silver nitrate from a known amount of metallic silver is employed, an exact determinate quantity of nitric acid will be set free, and, hence, the titration can be used for the standardising of acidimetric alkali solutions, the object with which the experiments were originally undertaken. The advantage of using pure metallic silver as the standard is obvious, but the difficulties referred to above, lying in the character of the precipitate, appear here also in an aggravated form. The attempt to titrate the free nitric acid without filtering from the silver cyanide meets with almost insuperable difficulties when the solution contains an excess of hydrocyanic acid.

In this case, as soon as the free nitric acid is neutralised, the complex salt, potassium argentocyanide, $KAgCy_2$, begins to form in accordance with the reaction—

$$HCN + AgCN + KOH = KAg(CN)_2 + H_2O.$$

Potassium argentocyanide is a neutral salt, so that the reaction of the solution changes from acid to neutral as excess of potassium hydroxide is added, instead of from acid to alkaline, and remains neutral until all hydrocyanic acid is converted into potassium argentocyanide. At the same time, the silver nitrate occluded in the precipitate slowly diffuses out, reacting as it does so with the hydrocyanic acid. It is therefore necessary to filter before titrating, and previous to the filtration a digestion for at least twenty-four hours is necessary, during which time the precipitate must be agitated with the solution. It is not thought worth while to give the details of the long series of experiments, since the final result is that the method, while capable of a high degree of accuracy when all precautions are observed, does not possess the simplicity which can be demanded of such a process.

It appeared to the writer to be a question as to how far the completeness of the reaction between hydroycanic acid and silver nitrate is due to the insolubility of silver cyanide, and how far to its being, possibly, a compound not subject to electrolytic dissociation; that is, not a true salt at all. If the latter were the dominant factor, it should be possible to secure a practically complete reaction between mercuric nitrate or chloride and hydrocyanic acid, since mercuric cyanide is well known to be a non-dissociated compound. If methyl orange is added in small quantity to a solution of pure mercuric chloride and also to a solution of hydrocyanic acid, both solutions remain pure yellow, showing no trace of acid reaction. If the solutions are now mixed together, they turn bright red. The experiment makes a striking lecture experiment illustrative of the theory of electrolytic dissociation. Nitrophenol, lacmoid paper, or even a rather insensitive, strongly blue, litmus-paper, can be used instead of methyl orange to show the liberation of hydrochloric acid, *i.e.*, the production of hydrogen ions. The reaction—$HgCl_2 + 2HCN = Hg(CN)_2 + 2HCl$, is not instantaneous, but is practically complete, and the disturbing factors mentioned above as occurring in the reaction between silver salts and hydrocyanic acid are absent. It appears, therefore, probable that silver cyanide also is a non-dissociated compound, and that the so-called "elective affinity" between cyanogen and silver is a phenomenon due to this fact rather than to the low solubility of silver cyanide, a supposition with which the known fact that an alkali cyanide reacts quantitatively with silver chloride to form silver cyanide is in the best of harmony.

The possibility of the application of these relationships to the acidimetric titration of mercury or of hydrocyanic acid and the cyanides lies very near. In the sequel it is shown that the possibility can easily be realised. It may be said that no new method for the titration of hydrocyanic acid is needed, since that of Liebig (*Liebig's Ann. Chem.*, 1851, lxxvii., 102), as modified by Deniges (*Ann. Chim. Phys.*, 1895 [7], vi., 381), answers all practical requirements. It is to be noted, however, that the application of Liebig's method requires a perfectly clear solution, whereas pharmaceutical preparations of hydrocyanic acid are frequently turbid. The addition of a new and convenient method of titration to the small number of those already known for the determination of mercury cannot be regarded as a work of supererogation, especially when the new method, as is the case with that described, is applicable to the determination of mercuric chloride in the highly dilute solutions of that substance employed by surgeons.

Determination of Hydroycanic Acid and Cyanides.

For this determination the following solutions are required:—*a*, decinormal solutions of hydrochloric acid and of potassium (or sodium) hydroxide; *b*, a nearly saturated solution of mercuric chloride, containing about 40 grms. of the pure re-crystallised salt per litre. The exact strength of this solution need not be known; *c*, a saturated solution of pure paranitrophenol in water. This is to be preferred to the solution in alcohol often recommended as an indicator. The aqueous solution keeps indefinitely in the light or in the dark.

To determine hydrocyanic acid or a simple cyanide, dilute the solution till it contains not more than about 1 per cent of hydrocyanic acid and add 2 drops of nitrophenol solution. If this imparts a yellow colour, add decinormal hydrochloric acid until the colour has all but disappeared; if it is colourless, add decinormal potassium hydroxide till the solution shows a very pale yellow. Now, add an excess of the mercuric chloride solution (usually 15 or 20 c.c.), stir and allow to stand for one hour at the temperature of the air.

A solution of hydrocyanic acid which had by gravimetric analysis been found to contain 3·40 per cent, was analysed by the above method. For that purpose, 50 c.c. was measured by a pipette into a 500 c.c. flask, filled to the mark, and shaken. Five c.c. of this solution were mixed with 10 c.c. of an approximately decinormal mercuric chloride solution, allowed to stand for an hour, and then titrated as described. Required, 6·30 c.c. of N/10 KOH, equivalent to 0·01704 grm. of hydrocyanic acid, or 3·408 per cent found.

Twenty c.c. of the same solution were mixed with 10 c.c. of an approximately 4 per cent mercuric chloride solution, and the liquid allowed to stand three hours. Required, 25·03 c.c. of decinormal potassium hydroxide, equivalent to 0·0677 grm. of hydrocyanic acid, or 3·385 per cent (on original solution) found.

From the original solution was prepared, by suitable dilution, a semi-normal hydrocyanic acid solution, containing, by calculation, 13·52 grms. per litre. Five c.c. of this solution were mixed with 33 c.c. of the last-mentioned mercuric chloride solution, and, after standing fifteen minutes, were titrated in the usual way. Required, 24·78 c.c. of decinormal potassium hydroxide, equivalent to 0·06703 grm. of hydrocyanic acid, or 1·34 per cent found. The small deficit observed here is probably due to a slight volatilisation of hydrocyanic acid during the manipulations incidental to dilution and exposure.

Determination of Mercury.

The only solution required, in addition to those mentioned above, is an approximately normal solution of hydrocyanic acid neutral to nitrophenol. Such a solution may be conveniently prepared in the following way without distillation: —Dissolve 68 to 80 grms. of the best commercial potassium cyanide in 0·5 litre of water, add about 5 grms. of barium chloride in saturated solution, and filter, thus removing carbonates which would interfere with the exact neutralisation. To the filtrate add about 10 c.c. of the nitrophenol solution (*vide supra*), and then dilute sulphuric acid till the yellow colour has become pale, finishing the neutralisation with decinormal hydrochloric acid. Finally, make up to a litre, disregarding the barium sulphate, which may be allowed to subside. This solution should contain about 27 grms. of hydrocyanic acid, and be colourless.

The mercury to be determined must be present as mercuric chloride (or bromide ?) If in the form of nitrate, a small excess of sodium chloride is added. Organic acids must be absent. It is next to be made neutral by addition of nitrophenol, avoiding undue excess, and hydrochloric acid, till the yellow colour is just on the point of disappearing. To the solution so prepared an excess of the neutral hydrocyanic acid solution is added, and the mixture set aside for not less than one hour for the completion of the reaction. The hydrochloric acid formed is titrated with potassium hydroxide, decinormal or centinormal, according to the dilution of the mercuric solution, until a permanent pale yellow tint is visible. A very small excess of hydrocyanic acid suffices, and an unnecessary excess is for obvious reasons to be avoided. To be sure that sufficient hydrocyanic acid is present, if in doubt add a few drops at the conclusion of the titration. This will instantly destroy the yellow colour if insufficient had been present, but otherwise will not affect it. The method has been repeatedly used by students in this laboratory with very satisfactory results, in part for the determination of mercuric chloride in solutions containing one part in ten thousand. They have with it obtained much better results than by the method of Vitali (*Bollettino Chimico Farmaceutico*, 1894, 365) for the examination of dilute solutions, and in considerably less time. Vitali's method consists in boiling the mercuric chloride solution with an excess of sulphurous acid, expelling the excess, and titrating acidimetrically the sulphuric and hydrochloric acids formed. The method is satisfactory for stronger solutions of mercuric chloride, but certain sources of error which are inappreciable in concentrated solution become serious when the solution is highly dilute. These are oxidation of the sulphurous acid by the atmosphere, imperfect expulsion of the last traces of sulphurous acid, reduction of the mercury too far; *i.e.*, to metal. Prolonged boiling is needed to drive off the last of the sulphur dioxide, which passes off rapidly at first, but with extreme slowness when only a little is left. Reduction of the mercurous chloride to metal is hindered by the considerable amount of hydrochloric acid present in more concentrated solutions, but in those of high dilution the amount of acid is insufficient to have this effect. The precipitate in the latter case often becomes grey. All these sources of error lead to the results of the determination being too high.

That the cyanide method also gives correct results with more concentrated solutions is shown by the following test analyses:—

A solution was prepared containing 6·780 grms. of pure mercuric chloride in 500 c.c. It was perfectly neutral to nitrophenol. To 5 c.c. of it, 2 c.c. of a hydrocyanic acid solution (3·4 per cent) was added, and 1 drop of nitrophenol solution. Required, 5 c.c. of decinormal potassium hydroxide, equivalent to 0·0678 grm. found. Twenty-five c.c. of the same solution, with 5 c.c. of hydrocyanic acid, required 25 c.c. of the standard alkali, equivalent to 0·339 grm. of mercuric chloride found. Again, 25 c.c. of the same solution, with 10 c.c. of hydrocyanic acid and 100 c.c. of water, required 25·03 c.c. of the hydroxide, equivalent to 0·3394 grm. of mercuric chloride found.

Since mercuric chloride is a substance which can be easily obtained in a high state of purity and is in every way well defined, it is suited as a standard for acidimetric solutions, the sharpness of the method of titration which has been described making it readily available for this purpose.

The results quoted of themselves show the practicability of this method, of which I shall have something more to say in connection with a discussion of other methods of standardisation.—*American Chemical Journal*, xxix., No. 3.

ON CERTAIN DERIVATIVES OF PICRIC ACID.*

By C. LORING JACKSON and R. B. EARLE.

THE following paper contains a description of some new compounds, not of much importance, which were prepared in our work upon the coloured addition-compounds formed from sodic alcoholates and nitro derivatives of benzol.

Picryl Bromide (1 - *Brom* - 2,4,6 - *trinitrobenzol*), $C_6H_2Br(NO_2)_3$.—This substance was prepared in the hope that it would lead to trinitroanisol with less trouble than the common way of making it from picryl chloride. The yield, however, was so small that the method did not prove of value. The process for making trinitroanisol from anisic acid, on the other hand, gave excellent results, and is described in our paper on the coloured addition-compounds.

Twenty-five grms. of 1-brom-2,4-dinitrobenzol were added to a mixture of 500 c.c. of fuming nitric acid, of sp. gr. 1·51, and 200 c.c. of fuming sulphuric acid, of sp. gr. 1·86, and the whole boiled vigorously for about three hours in a flask closed with a glass bulb. At the end of this time most of the nitric acid had been driven off, and the liquid ceased to boil quietly, but began to effervesce slightly, and to give off very dark red fumes. It was then allowed to cool, poured into a large volume of ice-water, and the precipitate formed dried on a porous plate to get tid of adhering oily impurities. The solid was re-crystallised from a mixture of alcohol and benzol until it showed the constant melting-point 122° to 123°, when it was dried at 100°, and analysed with the following result:—

0·2820 grm. substance gave, by the method of Carius 0·1824 grm. argentic bromide.

	Br.
Calculated for $C_6H_2Br(NO_2)_3$	27·37
Found	27·52

The yield was small, not more than 25 per cent of the theoretical, which we ascribe to oxidation during the long boiling, but, if an attempt was made to check this by diminishing the length of the boiling, little or none of the substance was formed. That it is really the picryl bromide was proved by its conversion into trinitroanisol, melting-point 64°, by treatment with sodic methylate.

Properties of Picryl Bromide.—It crystallises from alcohol in large, yellowish-white crystals, consisting of long plates terminated at each end by two planes at an acute angle, which is often truncated. Rhombic plates were also observed. Frequently arborescent, frost-like groups occur,

* The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Science, by R. B. Earle.

with many branches set obliquely to the trunk, and each branch bordered with rhombic plates, giving it a jagged outline. It melts at 122° to 123°, and is freely soluble in benzol or acetone; soluble in alcohol, cold or hot, chloroform, ether, methyl alcohol, glacial acetic acid, or carbonic disulphide; slightly soluble in cold, soluble in hot ligroin; insoluble in water. The strong acids do not act upon it even when hot, nor do cold alkalis affect it, but it is easily attacked by hot solutions of an alkali. Sodic methylate converts it into trinitroanisol, as has been already stated. The best solvent for it is a mixture of alcohol and benzol.

Phenyl Picrate, $C_6H_2(NO_2)_3OC_6H_5$.—A solution of sodic phenylate was prepared by dissolving 0·4 grm. of sodic hydrate in 1·2 grms. of phenol mixed with a little water; 2·6 grms. of picryl chloride were then added to this solution in small quantities at a time, stirring the liquid constantly during the addition. The mass soon took on a dark colour, and much heat was developed. On washing the product with water, a dirty, insoluble mass was obtained, which was crystallised from a mixture of alcohol and benzol until it showed the constant melting-point, 153°, when it was dried at 100°, and analysed with the following result:—

0·1676 grm. substance gave 20·2 c.c. N at 20° and 769·3 m.m.

	N.
Calculated for $C_6H_2(NO_2)_3OC_6H_5$	13·77
Found	13·96

Properties of Phenyl Picrate.—It crystallises from a mixture of alcohol and benzol in yellowish, short, thick prisms, probably of the monoclinic system, which are terminated by two planes at an obtuse angle. It melts at 153°, and is freely soluble in benzol or acetone; soluble in methyl or ethyl alcohol, chloroform, or cold glacial acetic acid, freely soluble in the last when hot; slightly soluble in ether; insoluble in water or ligroin. The best solvent for it is a mixture of alcohol and benzol. Willgerodt prepared this substance, but gives no description of it (*Ber.*, 1879, xii., 1278).

Action of Acetoacetic Ester on Phenyl Picrate.—In an earlier paper (*Am. Chem. Journ.*, xvii., 597) from this laboratory it was shown that the phenoxy groups in dichlordiphenoxyquinone were easily replaced by malonic ester residues; in fact, this gave the best method of preparing the dichlorquinonedimalonic ester. The following experiment was tried to see whether the phenoxy group in the phenyl picrate would also be susceptible of replacement:—A solution of sodic acetoacetic ester was prepared by adding 0·22 grm. of acetoacetic ester to the solution of sodic ethylate from 0·04 grm. of sodium and absolute alcohol, and to this was added a benzol solution of 0·5 grm. of phenyl picrate. The mixture took on a deep-red colour almost immediately, but we do not feel certain whether this was due to the salt of the picrylacetoacetic ester or to the formation of an addition-product (salt of a quinolnitro acid). The mixture was allowed to stand twenty-four hours at ordinary temperature, after which it was washed with water in a separating-funnel, and the aqueous washings acidified with dilute hydrochloric acid. The oily precipitate thus obtained was re-dissolved in sodic hydrate, filtered and acidified once more. As the precipitate was still gummy, it was extracted with carbonic disulphide, the extract evaporated to dryness, washed with a little cold alcohol, and re-crystallised from alcohol until it showed a constant melting-point. As this lay at 97° to 98° there can be no doubt that the substance is the trinitrophenylacetoacetic ester discovered by Dittrich (*Ber.*, 1890, xxiii., 2720), and that the phenoxy group is easily replaced by the acetoacetic ester residue.

4-Brom-2-nitrophenyl Picrate, $C_6H_2(NO_2)_3OC_6H_3BrNO_2$.—Two grms. of the sodium salt of 4-brom-2-nitrophenol were dissolved in 50 c.c. of hot alcohol, and 2 grms. of picryl chloride were added to the solution in small portions at a time, with constant stirring. The heavy, yellow, crystalline precipitate formed was filtered out, washed with water, and re-crystallised from acetone, until it showed the constant melting-point, 232°, when it was dried at 100°, and analysed with the following result:—

0·2009 grm. substance gave, by the method of Carius, 0·0885 grm. argentic bromide.

	Br.
Calculated for $C_6H_2(NO_2)_3OC_6H_3NO_2Br$.	18·63
Found	18·75

Properties of 4-Brom-2-nitrophenyl Picrate.—It crystallises from acetone in short, thick prisms, probably belonging to the monoclinic system, terminated at each end by two planes at an obtuse angle to each other. Its colour is yellowish-white, and it melts at 232°. It turns brown on exposure to the air. It is freely soluble in hot acetone, soluble in it when cold; soluble in hot benzol, slightly soluble in cold; slightly soluble in ethyl or methyl alcohol, chloroform, ether, or glacial acetic acid; insoluble in water or ligroin. The best solvent for it is acetone. It seems to form a coloured addition compound with sodic acetoacetic ester, but this may be instead the red salt of picrylacetoacetic ester, as pointed out in the last section.—*American Chemical Journal*, xxix., No. 3.

THE VOLUMETRIC DETERMINATION OF MANGANESE IN IRON AND STEEL.

By HARRY E. WALTERS.

In the *American Chemical Society Journal*, 1902, xxiv., 1206) there appeared an article by Stehman entitled "The Determination of Manganese in Iron and Steel," in which the author stated that in attempting to replace lead peroxide with ammonium persulphate and titrating with sodium arsenite, the silver salt of course caused trouble. If, however, the silver salt is thrown out of solution before the titration is begun, as insoluble silver chloride, the determination of the permanganic acid by a standard solution of sodium arsenite may be readily accomplished.

With the exception of the titration the method is the same as that read by me before this Section in September, 1901. While preparing that method the writer also tried to make a titration method, but without success, as the hot solutions were titrated and the reaction between the excess of persulphate and the silver nitrate caused the results to be high and irregular.

Since the article by Stehman appeared I have doubted the necessity of precipitating the silver as chloride if the solution be cooled before the titration is begun.

In order to prove the correctness of this view a number of samples were taken and treated as follows:—

0·2 grm. of the samples and a standard steel of known manganese contents were weighed off into suitable test-tubes or beakers, and 10 c.c. of nitric acid of 1·20 sp. gr. were added to each. The solutions were heated until the samples were dissolved and all nitrous fumes were driven off. Fifteen c.c. of a solution of silver nitrate equal to 0·02 grm. $AgNO_3$ (1·33 grms. of the salt to 1 litre of water) were added to each. About one-half grm. ammonium persulphate salt was added, and the solutions were heated until the oxidation commenced, and then for about half a minute longer. The solutions were then cooled.

In preparing the iron samples 1 grm. was dissolved in 30 c.c. of nitric acid of 1·20 sp. gr., filtered into 100 c.c. calibrated flask, and diluted to the mark. After thorough mixing 20 c.c. of the solution were transferred to test-tubes or beakers, and a little ammonium persulphate salt added to destroy the combined carbon. Five c.c. of a solution of silver nitrate (4 grms. of the salt to 1 litre of water) and a little more persulphate were added, and the procedure continued the same as for steels.

When the permanganic acid solutions were cold they were treated as follows:—

First Series.—The manganese was estimated colorimetrically.

Second Series.—The silver was precipitated as chloride and the solutions were then titrated with a sodium arsenite solution until the pink colour was destroyed.

Third Series.—The solutions were titrated with sodium arsenite without precipitating the silver as chloride.

Fourth Series.—The solutions were titrated with hydrogen peroxide without precipitating the silver as chloride.

The following results were obtained :—

Steel No.	18 ..	0·28	0·27	0·28	0·27
,,	17 ..	0·47	0·46	0·48	0·47
,,	11 ..	0·53	0·55	0·54	0·53
,,	22 ..	0·57	0·59	0·59	0·59
,,	26 ..	0·40	0·44	0·43	0·43
,,	33 ..	0·49	0·49	0·49	0·49
,,	90 ..	0·90	0·92	0·90	0·89
,,	47 ..	0·43	—	0·43	0·43
Iron, S	..	0·19	—	0·21	0·19
,,	712 ..	0·22	—	0·22	0·21
,,	713 ..	0·23	—	0·23	0·24
,,	716 ..	0·24	—	0·24	0·24
,,	828 ..	0·16	—	0·16	0·15
,,	813 ..	0·13	—	0·11	0·11
,,	829 ..	0·18	—	0·17	0·19
Steel No.	68 ..	0·73	0·72	0·74	0·74

It will be observed that the results all agree closely whether the silver was separated or not, and that hydrogen peroxide (as was to be expected) may be used as well as the sodium arsenite.

The end-point in all these titrations is not as sharp as might be desired, but I think it is sharper if the silver is not precipitated.

If the silver is not precipitated the titration must be done quickly, as the persulphate and silver nitrate in solution react to reproduce the colour if allowed to stand.—*Proceedings of Engineers' Society of Western Pennsylvania*, xix., No. 7.

THE PREVENTION OF BUMPING.

By HEYWARD SCUDDER.

A SINGLE glass capillary tube when used according to the following directions will stop most cases of bumping that occur in ordinary laboratory work. The method is simple, effective, and introduces into the liquid no foreign substance except glass and one small bubble of air. In order to carry it out successfully the following details of procedure must be carefully observed.

The origin of the use of a capillary is obscure. The earliest published reference that I have found is by Gernez (*Comptus Rendus*, lxxxvi., 472). Since these references are only incidental and therefore difficult to find, it is quite possible that there may be an earlier one. I have tried all the methods published (most of which are only for special cases), and have found none so simple or of such wide application as the one presented here.

The capillary is made by drawing out a piece of glass tubing until the internal diameter is about 0·5 to 1 m.m. A seal is then made by holding the tube horizontally in the edge of the flame of a Bunsen burner, until the walls have melted together. The tube is bent, if necessary, or held horizontally till cold. For most purposes the seal should be about 1 c.m. from the open end of the tube. The tube is cut off at the desired length and the other end sealed to prevent the entrance of liquid. When cold, the tube is placed open end down in the liquid to be boiled. The open end should rest on the bottom of the vessel containing the liquid, and should remain there during use. When liquids of high specific gravity are being boiled, it is necessary, therefore, to have the capillary so heavy that it will not be thrown off the bottom. This weight can be obtained by drawing out the tube from which the capillary is made only near the seal, or by using a very thick walled tube.

In a general way the theory of the action of such a tube is, that when heated the air in the capillary expands and passes through the liquid in bubbles. The vapour of the liquid gradually replaces the air, and the stream of bubbles is continuous as long as the temperature around the capillary is at the boiling-point of the liquid. This constant bubbling prevents superheating and consequent explosive boiling. It is apparent that the size of the bubble will depend chiefly on the on the width of the capillary. This should vary with the nature of the liquid. For liquids of low boiling-point or for frothing liquids a narrow capillary is best, while for heavy liquids a wider capillary (even as wide as 5 m.m. internal diameter) is more suitable.

When boiling with a return condenser, the seal of the capillary *must* be below the surface of the liquid. If the seal is above the surface, cold drops falling back from the condenser will strike the capillary and cause condensation of the vapour inside it, thus stopping the stream of bubbles. To prevent displacement, the capillary should be of such a length that the upper end reaches nearly to the top of the neck of the flask. When the liquid is in a thin broad layer the capillary should be bent at the seal so as to be parallel or nearly parallel to the bottom of the flask. In boiling liquids in a test-tube, care must be taken that the heat is applied at the bottom of the tube. When a solid is being dissolved, or when in the course of a reaction a solid is being precipitated out of solution, the capillary should be examined from time to time to see that the end has not become clogged.

The capillary is useless if completely filled. Therefore it must be cold and empty when placed in the liquid. Care should be taken (especially in the case of liquids that usually bump badly) to protect the flame from draughts, so that the temperature of the liquid shall not temporarily fall below the boiling-point, allowing the capillary to fill.

Other minor changes and precautions may be advisable at times, but it will be found that they depend on the following principles. The capillary must never be allowed to become filled with liquid. The greater the amount of air there is to drive out (depending on the width of the capillary and the distance from the seal to the open end), the longer will it take to get a rapid stream of bubbles of vapour of the liquid. The greater the distance from the seal to the open end, the longer will it take to fill the capillary on cooling.

This method has been in successful use in these laboratories for nearly a year. By its use it is possible to saponify esters by boiling with a 50 per cent solution of potassium hydroxide (using a return condenser) or to boil concentrated sulphuric acid in a test-tube without any bumping. Only two cases have been met with in which bumping persisted after the capillary was introduced. Both were reactions carried out with a return condenser. Although the bumping continued, it was so greatly lessened that the liquid was not thrown out of the upper end of the condenser, and there was no danger of having the flask broken.—*Journal of the American Chemical Society*, xxv., No. 2.

Estimation of Argon in Atmospheric Air.—Henri Moissan.—The author makes use of the property metallic calcium possesses of absorbing all the oxygen and nitrogen in a given volume of air, in order to estimate the argon in various samples of air. He finds that specimens obtained from the interior of continents at altitudes of 0 to 5800 metres contain from 0·932 to 0·935 per cent by volume of argon, a remarkably constant proportion. Specimens from the surface of different seas contain quantities of argon which in general vary more, and are slightly higher than those from inland parts. A single sample taken over the Atlantic Ocean contained 0·9492 per cent of argon.—*Comptes Rendus*, xxxvii., No. 16.

NOTICES OF BOOKS

Physical Chemistry in the Service of the Sciences. By Jacobus H. van't Hoff. English Version by Alexander Smith. Chicago: The University of Chicago Press. 1903.

The debt which the scientific world owes to Prof. van't Hoff, especially in the domain of physical chemistry, is so thoroughly recognised that any lectures given by him will command the interest of a vast number of readers of all nationalities. These nine lectures were delivered in June, 1901, at the invitation of the University of Chicago on the occasion of the decennium of its foundation, and are here reproduced only slightly condensed and with very few alterations from the stenographic report. The subject was divided by the lecturer into four parts. An introductory lecture, before a general educational conference, gave some explanation of the scope and aims of physical chemistry. The subsequent lectures dealt in pairs with its relations to other branches of science and its application to the solution of many problems connected with them. Thus the first two explained the great services it has rendered in the region of pure chemistry, taking as an illustration the study of the changes which carnallite undergoes in presence of water when the temperture is altered, and touching upon the growth of Arrhenius's theory of electrolyte dissociation. The application to the technical problems of industrial chemistry dealt with the study of the phenomenon known as tin disease, and also the behaviour of carboniferous iron, which is graphically represented in a diagram. Under the heading of Physiology the lecturer explained, first, the importance of the theory of solutions, including a short mention of Loeb's work on artificial fertilisation, and, secondly, the chemical changes brought about by enzymes, the fuller investigation of which subject seems to be destined to lead to such exceedingly interesting and valuable results. Finally, the application of physical chemistry to geology introduced the study of the conditions of formation of geological salt deposits.

The French edition ("La Chimie Physique et ses Applications." Paris: Librairie Scientifique A. Hermann) has been prepared from the German by Prof. A. Corvisy. The excellent portrait of the author, which appears as a frontispiece in the English edition, and the plate showing the appearance of a sheet of tin attacked by the tin disease do not appear in the French translation.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Edited by Franz Hofmeister. Band IV. 7 and 8 Heft. Braunschweig: Friedrich Vieweg und Sohn. 1903.

The articles in this number of these *Beiträge* have been contributed by well-known authors, and are full of interest for those engaged in the study of physiological chemistry. Dr. Carl Oppenheimer sends two communications, one written in collaboration with Dr. Hans Aron, on the behaviour of genuine serum towards tryptic digestion, and another on the fate of albuminous substances in the animal body. The results of exhaustive investigations on the precipitation of colloids are described by K. Spiro. In this research the effects of the addition of salt solutions, alcohols, and alcoholic solutions of salts were minutely examined, and are here detailed. A second and third communication on the application of chemical methods of investigation to the lymphatic organs occupies a large part of the number, which also contains a short paper relating to the derivatives obtained from taurine by the action of benzoic anhydride, phthalic anhydride, and other substances. The author, Dr. Siegfried Tauber, found that sodium cholate under suitable conditions acts on taurine, giving rise to a substance the analysis of which did not show great differences from that of taurocholic acid, and was hence led to the conclusion that he had produced a body which was either identical or isomeric with that acid.

Le Point Critique des Corps Purs. ("The Critical Point of Pure Bodies"). By E. Mathias. Paris: C. Naud. 1903.

This book contains a very comprehensive treatment of the subject, and owing to its temperateness and impartiality deserves to be regarded as an excellent example of what a monograph should be. It opens with an account of Andrews' pioneering work and his classical theory, and thence passes to the description and criticism of the various experimental methods of determining the critical pressure, volume, and temperature, the importance of the optical method of fixing the temperature and density being marked by the specially full treatment accorded to it. Methods of calculation of the critical constants have been carefully examined, and a table is added containing the constants for some 165 substances, mostly belonging to organic chemistry. Since the book aims at sifting evidence and deciding moot points, ample scope is given for the expression of the author's individual opinion, and it must be admitted that he appears to have always stated the case and his views of it with the utmost fairness and justice. The work gives an excellent account of the present state of our knowledge, and the researches which are being carried out to supplement it.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 15, October 12, 1903.

Temperature of Ignition and Slow Combustion of Sulphur in Oxygen and Air.—Henri Moissan.—The ignition temperature of sulphur is 282° in oxygen and 363° in air, both at atmospheric pressure. However, the combustion or slow combination of sulphur with oxygen takes place at a temperature much below that of ignition. Thus, at 100°, this union is manifest after twelve hours. A quantity of sulphur dioxide is produced which, when cooled to −186°, can be obtained in the solid state and identified. This delicate experiment allows of an investigation regarding the phenomenon of combustion with the different varieties of sulphur, even at ordinary temperatures, and it leads to the conclusion that all sulphur, when exposed to air, burns very slowly, giving traces of sulphurous anhydride. The author's series of experiments extend his former researches, and prove that substances such as carbon and sulphur do slowly burn in air at temperatures far removed from their ignition-points.

Electrification of Contact, and Theory of Colloidal Solutions.—Jean Perrin.—It is probable that all colloidal solutions are formed of granules invisible with the microscope, but larger than molecules. The author investigates the causes which assure a stable equilibrium for a certain diameter of molecule, and he proposes a theory that the superficial tension and cohesion tend to the increasing of a granule, but the electrification of such a granule is an internal cause of dislocation, and it may be conceived that there exists a particular diameter for which these two opposing influences are in equilibrium.

A Series of Bismuth Compounds.—G. Urbain and H. Lacombe,—The authors make a series of experiments which show the analogy between bismuth and the rare earths. They find that bismuth bears the same relation to the rare earths that zinc does to magnesium. A new series of bismuth nitrates are prepared, whose general formula is $3M'(NO_3)_2.2Bi(NO_3)_3.21H_2O$.

Action of Carbon Dioxide on the Metallic Phosphates under Pressure.—A. Barillé.—The author's ex-

periments prove that when the tribasic phosphates of sodium, ammonium, calcium, barium, and magnesium combine with carbon dioxide under pressure in presence of water, a bibasic phosphate and the corresponding bicarbonate are formed. These results are only obtained after evaporation of the carbonic solution either *in vacuo* or at a moderate temperature. The reaction is shown by the following equation :—

$$2(PO_4.M'_3)+4CO_3H_2 = \underbrace{(PO_4.M'_2H)_2\ 2CO_2,2(CO_3HM')}_{\text{Tribasic carbono-phosphate.}}+2H_2O\ ;$$

then, further, by dissociation—

$$(PO_4M'_2H)_2\ 2CO_2,2(CO_3HM) = 2(PO_4M'_2H)+2(CO_3HM)+2CO_2.$$

The carbonophosphates only exist in solution, and even in this state they always rapidly dissociate when in contact with air.

Estimation of Vanadium in Metallurgical Products. —Em. Campagne.—The methods by which vanadium is estimated in the alloys and minerals may be considerably simplified, besides gaining in exactness, by the following modifications :—(1) The ether charged with hydrochloric acid dissolves ferric chloride, whilst it leaves the vanadium oxychloride undissolved ; (2) the oxychloride, $VOCl_3$, is reduced to $VOCl_2$ by prolonged boiling with hydrochloric acid, whilst the ferric chloride is not altered. By transformation of the chlorides into sulphates, blue di-vanadyl sulphate, $V_2O_2(SO_4)_2$, is obtained, and ferric sulphate. By titration with permanganate, the quantity of oxygen necessary to transform di-vanadyl sulphate into vanadic sulphate, $V_2O_2(SO_4)_3$, can be found, and from this the amount of vanadium present in the solution estimated. The reactions may be expressed by the following equations :—

$$V_2O_5+6HCl = 2VOCl_2+3H_2O+Cl_2,$$

$$2VOCl_2+2H_2SO_4 = V_2O_2(SO_4)_2+4HCl,$$

$$5[V_2O_2(SO_4)_2]+2KMnO_4+8H_2SO_4 = 5[V_2O_2(SO_4)_3]+K_2SO_4+2MnSO_4+8H_2O.$$

Nitric Ethers of Acid Alcohols.—H. Duval.—The author investigates the series of acid alcohols, and prepares the nitrates of the acid alcohols of the fatty series possessing either substituted halogen radicles or not ; he then observes their method of decomposition ; and, finally, examines the transformation of the nitrotartric ethers into nitrotartronic ethers.

Abnormal Fixation of Trioxymethylene on to certain Aromatic Organo-magnesium Derivatives. — M. Tiffeneau and R. Delange.—The authors investigate the reaction between trioxymethylene and magnesium benzyl chloride, by which a crystalline alcohol is obtained.

Action of Mixed Organo-magnesium Compounds on Amides. New Preparation of Ketones. — Constantine Béis.—When an amide is added to an excess of a mixed organo-magnesium compound, and the whole heated for some hours on a water-bath, ketones are produced. The series of reactions which take place is represented by the following equations, in which R and R' are the alcoholic radicles and X is a halogen :—

1. $R{-}CONH_2+2Mg\begin{matrix}R'\\X\end{matrix} \quad R{-}C\begin{matrix}OMgX\\NHMgX\\R'\end{matrix}+R'{-}H.$

2. $R{-}C\begin{matrix}OMgX\\NHMgX\\R\end{matrix}+2H_2O = R{-}C\begin{matrix}OH\\NH_2\\R'\end{matrix}+MgX_2+Mg(OH)_2.$

3. $R{-}C\begin{matrix}OH\\NH_2\\R'\end{matrix} = R{-}CO{-}R'+NH_3.$

MISCELLANEOUS.

Combined Chemical and Physical Bench.—Messrs. W. and J. George, of 33—37, Hatton Wall, E.C., have recently introduced a combined chemical and physical bench, to meet the growing demand for such in small institutions where space is a consideration and separate rooms cannot be provided for the two subjects. Hitherto the construction of combined chemical and physical benches has only permitted the shelves to be removed for physical work, and it was often difficult to find room for them off the table. Moreover, the risk of carrying a number of shelves containing chemical reagent bottles was considerable. The new form of bench entirely does away with these drawbacks, the shelves being so arranged that, by reversing a catch, they rise up into position when required for chemical work, and by simply pressing them on the top they descend, leaving the table clear for physical experiments. The ordinary drawers and cupboards are of the usual size, and no space is wasted.

Fractional Combustion of Hydrogen, Carbonic Oxide, and Isopentane.—K. V. Charitchkof.—The author has shown previously that Winkler's method of fractional combustion is inapplicable to the analysis of natural gas. In the actual experiment he determines the temperatures of the combustion of pure hydrogen, of isopentane either pure or mixed with hydrogen, and of hydrogen mixed with carbonic oxide. The apparatus has been modified slightly ; a thread of palladium-coated asbestos is placed in a tube in the form of a V, which is plunged into an oil-bath, or one of paraffin or tin, according to the temperature it is desired to reach. According to the amount of CO_2 formed, the proportion of isopentane or of carbonic oxide burnt is calculated. The results are given in tables, from which the following conclusions are deduced :—1. Pure hydrogen burns completely at 80°, pure carbonic oxide at about 290°, and isopentane above 395°. 2. The temperature of combustion is the same whether oxygen or air be used ; the presence of nitrogen or any other inert gas is without influence on the temperature of combustion. 3. The addition of carbonic oxide or of isopentane raises the temperature of combustion of hydrogen ; the influence of carbonic oxide is the greater, although this gas burns at a much lower temperature than isopentane. 4. In a mixture of equal volumes of hydrogen and isopentane, the hydrogen is completely burnt at about 200°, but a proportion of isopentane, varying from 1·6 to 9·2 per cent, is also burnt. 5. The rate of combustion of isopentane is very low ; to burn the whole of this gas it is necessary to pass it through the tube containing the palladium-coated asbestos several times. 6. Carbonic oxide behaves almost like isopentane ; its presence raises the temperature of combustion of hydrogen as it is present in greater proportion. These results, and, above all, the change of the temperature of combustion of the hydrogen, brought about by the presence of less easily combustible gases, show clearly the inapplicability of Winkler's method.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 461.

Sub-oxides of Cadmium.—S. Tanatar and M. Lévine. —In a previous paper one of the authors has described a sub-oxide, Cd_4O, obtained by heating oxalate of cadmium in a current of CO_2. To obtain other sub-oxides, the authors have prepared a basic oxalate by mixing molecular quantities of the neutral oxalate with the oxide CdO ; the product obtained has the characteristics of a basic salt and not of a mixture. When heated in a tube closed at one extremity it decomposes, as shown by the analysis of the gases given off and of the residue, according to the following equation : — $3(C_2O_4Cd+CdO) = 2Cd_3O_2 + 5CO_2 + CO$. Cd_3O_2 is a deep green coloured powder ; dilute hydrochloric acid dissolves it with the deposition of metallic cadmium, $Cd_3O_2+4HCl = 2CdCl_2+2H_2O+Cd$. It is not a mixture of CdO and Cd, as when shaken up with mercury it does not give up a trace of cadmium ; it may be looked upon as a compound of CdO with Cd_2O. When heated away from

the air it decomposes into CdO and Cd; in the presence of water it decomposes rapidly into $Cd(OH)_2$ and Cd. By mixing 2 molecules of the neutral oxalate of Cd with 1 molecule of CdO, the authors obtained another basic salt; at least, this appears to be probable. This salt is destroyed by heat, and leaves as a residue a green powder resembling the sub-oxide, Cd_3O_2, but the analysis of the gases given off, and of the residue, shows that the reaction takes place according to the equation—

$$2(2C_2O_4Cd + CdO) = 3Cd_2O + 7CO_2 + CO.$$

Treated with dilute hydrochloric acid, Cd_2O leaves a deposit of Cd, more considerable than the oxide, Cd_3O_2:—$Cd_2O + 2HCl = CdCl_2 + H_2O + Cd$. The authors have made a thermochemical examination of these sub-oxides.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 495.

Contribution to the Study of the Inert portion of the Atmosphere.—A. Lidof.—The author estimates the nitrogen in the air by the method of direct absorption already described (*Bull. Soc. Chim.*, vol. xxi., p. 862). From a large number of determinations he arrives at the following conclusions:—1. The composition of the inert portion of the atmosphere undergoes variations which, in certain exceptional cases, may reach 7 or 8 per cent by volume. 2. The most marked and unexpected variations are met with in the autumn. 3. When the soil is frozen, so that there is no longer any exchange between the atmospheric air and that entangled in the soil, the composition of the air remains much more constant. 4. Sometimes an amount of nitrogen is found much higher than the normal, reaching 80 per cent, and this cannot be explained by errors of analysis; it must be admitted that a compound of nitrogen is present in the air, and that it decomposes, giving up nitrogen, by the action of magnesium at a high temperature.—*Journ. Soc. Phys. Chim. R.*, xxxiv., 445.

Hypertungstic, Hyperuranic, and Hypervanadic Acids.—L. Pissarjevsky.—By the examination of solutions of tungstic acid containing H_2O_2 in the presence of ether, the author found that, besides the hypertungstic acid, $WO_3H_2O_2$, there is another, $WO_32H_2O_2$, and that by dissolution these acids are dissociated, losing H_2O_2 according to the equations:—

A. $WO_32H_2O_2 \rightleftarrows WO_3H_2O_2 + H_2O_2$,

B. $WO_3H_2O_2 \rightleftarrows WO_3 + H_2O_2$.

With a large excess of H_2O_2, the equilibrium A only takes place; if the concentration of the H_2O_2 is less, we have the equilibrium B. The Na salt of hyperuranic acid, $(Na_2O_2)UO_4$, dissociates in aqueous solution, forming H_2O_2. The dissolution of vananic anhydride, V_2O_5 in H_2O_2 forms a hypervanadic acid, HVO_4, which behaves as a strong acid. All the hyperacids which by the action of sulphuric acid form H_2O_2, may be considered as having the following constitutions:—$VO_2(O_2H)$, hypervanadic acid; $WO_2(OH)(O_2H)$, $WO_2(O_2H)_2$, hypertungstic acids; $MoO_2(OH)(O_2H)$, $MoO_2(O_2H)_2$, hypermolybdic acids; $UO_2(OH)(O_2H)$, hyperuranic acid; we might even regard them as H_2O_2 in which one H is replaced by a radical VO_2, $UO_2(OH)$, &c.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 472.

MEETINGS FOR THE WEEK.

WEDNESDAY, 18th.—Microscopical, 8. "Microscopic Re-solution," by Prof. J. D. Everett, F.R.S. "The Mouth Parts in the Nemocera, and their Relation to the other Families in Diptera," by Walter Wesché.

—— Chemical, 5.30. "Constitution of Ethyl Cyanacetate—Condensation of Ethyl Cyanacetate with its Enolic Form," by P. Remfry and J. F. Thorpe. "The Action of Water and Dilute Caustic Soda Solutions on Crystalline and Amorphous Arsenic," by W. T. Cooke. "The Union of Carbon Monoxide and Oxygen, and the Drying of Gases by Cooling," by A. F. Girvan. "Note on a Double Chloride of Molybdenum and Potassium," by G. G. Henderson. "Simplification of Zeisel's Method for the Determination of Methoxy- and Ethoxy-groups," by W. H. Perkin, sen. "The Action of Benzamidine on Olefine β-Diketones," by S. Ruhemann.

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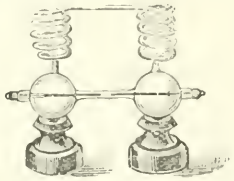

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2295.

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 236).

Chapter IV. (*continued*).

Theory of Radio-activity.

The following is, according to MM. Curie and Debierne, a very general theory which allows of the co-ordination of the results of the investigation of induced radio-activity, which results I have just stated, and which constitute facts apart from any hypothesis.

It may be said that each atom of radium acts as a constant and continuous source of energy, without actually defining the origin of this energy. The radio-active energy which accumulates in the radium tends to become dissipated in two different ways:—(1) By radiation (rays both charged and uncharged with electricity); (2) by conduction, *i.e.*, by gradual transmission to surrounding bodies in a medium ot gases and liquids (production of an emanation and transformation into induced radio-activity).

The loss of radio-active energy, both by radiation and by conduction, increases with the amount of energy accumulated in the radio-active body. The system is necessarily in equilibrium when the double loss of which I have just made mention compensates the constant gain due to the action of radium. This manner of regarding the subject is similar to that in use for calorific phenomena. If in the interior of any body there is, owing to any cause a continuous and constant evolution of heat, the heat accumulates in the body and the temperature rises until the loss of heat by radiation and conduction is in equilibrium with the constant gain of heat.

In general, except under certain special circumstances, the activity is not propagated through solid bodies. When a solution is kept in a sealed tube, the loss by radiation alone takes place, and the radiating activity of the solution is of a higher degree.

If, on the contrary, the solution stands in an open vessel, the loss of activity by conduction becomes considerable, and when the state of equilibrium is attained, the radiating activity of the solution is very feeble.

The radiating activity of a solid radium salt left exposed to the air does not sensibly diminish, because the propagation of activity by conduction not taking place through solid bodies, it is a very thin superficial layer only that produces induced radio-activity. The solution, however, of the same salt produces much more intense phenomena of induced radio-activity. With a solid salt the radio-active energy accumulates in the salt, and is dissipated chiefly by radiation. On the other hand, when the salt has been for several days in aqueous solution, the radio-active energy is divided between the salt and the water, and if separated by distillation the water carries with it a large portion of the activity, and the solid salt is much less active (ten or fifteen times) than before solution. Afterwards the solid salt gradually regains its original activity.

The preceding theory may be yet further defined by supposing the radio-activity of radium itself to be produced through the medium of the radio-active energy emitted in the form of an emanation.

Each atom of radium may be considered as a constant and continuous source of emanation. At the same moment that this form of energy is produced, it undergoes a progressive transformation into radio-active energy of the Becquerel radiation. The velocity of this transformation is proportional to the quantity of the emanation accumulated.

When a radium solution is placed within an enclosure, the emanation is able to expand into the enclosure and to spread out over the walls. Here it is, therefore, that it is transformed into a radiation, the solution giving off but few Becquerel rays; the radiation is, in some sort, *externalised*. On the other hand, with solid radium, the emanation not being able to escape readily, accumulates, and is transformed into the Becquerel radiation on the spot; this radiation therefore acquires a higher value.

If this theory of radio-activity were general, we should have to say that all radio-active bodies give rise to an emanation. Now this emission has been confirmed in the case of radium, thorium, and actinium; with the latter in particular the emission is enormous, even in the solid state. Uranium and polonium do not seem to emit any emanation, though they generate Becquerel rays. These bodies produce no induced radio-activity in an enclosed space, as do the radio-active bodies mentioned before. This fact is not in absolute contradiction to the preceding theory. If uranium and polonium were to emit emanations which become destroyed with very great rapidity, it would be very difficult to observe the carriage of such emanations by the air and the effects of induced radio-activity produced by them upon neighbouring bodies. Such a hypothesis is not improbable, since the times required for certain quantities of the emanations of radium and thorium to diminish to one-half are in the proportion of 5000 to 1. We shall see, moreover, that, under certain conditions, uranium can excite induced activity.

Another Form of Induced Radio-activity.

According to the law of dissipation in the open air of the activity induced by radium in solid bodies, the activity after one day is almost imperceptible.

Certain bodies, however, form exceptions; such are celluloid, paraffin, caoutchouc, &c. When these bodies have been acted upon to a sufficient degree, they lose their activity more slowly than the law can account for, and it is often fifteen or twenty days before the activity becomes imperceptible. These bodies appear to have the property of becoming charged with radio-active energy in the form of an emanation; they afterwards lose it gradually, causing induced radio-activity in the vicinity.

Induced Radio-activity with Slow Dissipation.

There is yet another form of induced radio-activity, which appears to be produced in all bodies which have been kept for months in an active enclosure. When these bodies are removed from the enclosure their activity at first diminishes to a very low value according to the ordinary law (diminution to one-half in half-an-hour); but when the activity has fallen to about 1/20,000 of the initial value, it diminishes no further, or at least it is dissipated very slowly, sometimes even increasing in amount. We have sheets of copper, aluminium, and glass which still retain a residual activity after six months.

These phenomena of induced radio-activity appear to be of a different kind from the ordinary ones, and show a much slower process of evolution.

A considerable time is also necessary both for the production and dissipation of this form of induced radio-activity.

Radio-activity Induced upon Substances in Solution with Radium.

When a radio-active ore containing radium is treated, with the object of extracting the radium, chemical separations are effected, after which the radio-activity is confined entirely to one of the products. In this way active products, which may be several hundred times as active as uranium, are separated from totally inactive products, such as copper, antimony, arsenic, &c. Certain other bodies (iron, lead) were never separated in an entirely inactive state. As

* Thesis presented to the Faculté des Sciences de Paris.

these active bodies are concentrated, the case is no longer the same; each chemical separation no longer furnishes absolutely inactive products; all the resulting products of a separation are active in varying degrees.

After the discovery of induced radio-activity, M. Giesel was the first to attempt to excite activity in ordinary inactive bismuth by keeping it in solution with very active radium. He thus obtained radio-active bismuth, and from this he concluded that the polonium extracted from pitchblende was probably bismuth made active by the vicinity of the radium contained in the pitchblende.

I have also prepared active bismuth by keeping bismuth in solution with a very active radium salt.

The difficulties of this experiment consist in the extreme precautions which must be taken to remove all traces of radium from the solution. If we realise what an infinitesimal quantity of radium suffices to produce very considerable radio-activity in 1 grm. of material, it is difficult to believe in the possibility of sufficiently washing and purifying the active product. Each purification causes a diminution of activity of the product, whether this be due to removal of traces of radium or that the induced radio-activity is, under these circumstances, not proof against chemical reactions.

The results I obtained appear, however, to establish with certainty the fact that the activity is produced and persists after the radium is removed. On fractionating the nitrate of my active bismuth by precipitation with water from the nitric acid solution, I found that after careful purifying it fractionated like polonium, the most active portion being precipitated first.

If the purification is not complete the opposite occurs, showing that traces of radium still remain. I thus obtained active bismuth which from the manner of fractionation showed great purity and which was 2000 times as active as uranium. This bismuth diminishes in activity with lapse of time. But another portion of the same product, prepared with the same precautions, and fractionating in the same manner, preserves its activity without diminution for actually a period of about three years.

This activity is 150 times as great as that of uranium.

I have also prepared active lead and silver by leaving them in solution with radium. Generally induced radio-activity obtained in this way scarcely lessens with lapse of time, but it does not as a rule withstand many successive chemical changes of the active body.

M. Debierne made active barium by placing it in solution with actinium. This barium remains active after several chemical reactions, its activity being therefore a somewhat stable atomic property. Active barium chloride fractionates like barium-radium chloride, the more active portions being the least soluble in water and dilute hydrochloric acid. The dry chloride is spontaneously luminous; its Becquerel radiation is similar to that of barium-radium chloride. M. Debierne has prepared an active barium chloride 1000 times as active as uranium. This barium, however, had not acquired all the characteristics of radium, for it showed none of the strongest radium lines in the spectroscope. Further, its activity diminished on standing, and after three weeks it had become one-third of its original value.

There is a wide field for research upon the radio-activity induced in substances in solution with active bodies. It appears that, according to the conditions of experiment, more or less stable forms of induced atomic radio-activity may be obtained. The radio-activity induced under these circumstances is perhaps identical with that form, which dissipates slowly, obtained by prolonged exposure at a distance in an active enclosure. We have reason to enquire to what degree induced radio-activity affects the chemical nature of the atom, and if it is able to modify the chemical properties of the latter, either temporarily or permanently.

The chemical investigation of bodies excited at a distance is rendered difficult by the fact that the induced activity is limited to a very thin superficial layer, and that, consequently, only a very small proportion of the material has been affected.

Induced radio-activity also results from leaving certain substances in solution with uranium. The experiment succeeded in the case of barium. If, as was done by M. Debierne, sulphuric acid be added to a solution containing uranium and barium, the precipitate of barium sulphate acquires radio-activity, and, at the same time, the uranium salts loses part of its activity. M. Becquerel found, after repeating this experiment several times, that almost inactve uranium was obtained. This might lead to the opinion that a radio-active body differing from uranium had been separated from the latter, its presence producing radio-activity in uranium. This, however, is not the case, for after some months the uranium regains its original activity; the precipitated barium sulphate, on the contrary, loses what it acquired.

A similar phenomenon is observed with thorium. Mr. Rutherford precipitated a solution of a salt of thorium with ammonia; he separated off the solution and evaporated it to dryness. He thus obtained a small very active residue, and the precipitated thorium was observed to be less active than before. This active residue, to which Mr. Rutherford gives the name of *thorium* X, loses its activity after a time, whilst the thorium regains its original activity.

Its appears, then, that concerning induced radio-activity all bodies do not behave in a similar manner, and that certain of them are much more readily excited than others.

Dissemination of Radio-active Particles and Induced Radio-activity of the Laboratory.

In making investigations of strongly radio-active bodies, particular precautions must be observed for obtaining delicate determinations. The different objects used in the chemical laboratory and those used for physical experiments soon acquire radio-activity, and act upon photographic plates through black paper. Dust particles, the air of the room, clothing, all become radio-active. The air of the room becomes a conductor. In our laboratory the evil has become acute, and we no longer have any apparatus properly insulated.

Special precautions must therefore be taken to avoid as much as possible the dissemination of active dust particles, and to avoid also the phenomena of induced activity.

The objects employed in chemistry should never be brought into the room where physical research is carried on, and as far as possible should be avoided any unnecessary keeping of active substances in this room. Before beginning our researches we were in the habit, in the case of electrical experiments, of making a connection between the different parts of the apparatus by insulated metallic wires, protected by metal cylinders connected to earth, which screened the wires from all outside electrical forces. In the investigation of radio-active bodies this arrangement is quite defective; the air being a conductor there is incomplete insulation between the thread and the cylinder, and the inevitable electromotive force of contact between the thread and the cylinder tends to produce a current through the air, and to cause a deflection of the electrometer. We now screen all the wires from the air by placing them inside cylinders filled with paraffin or other insulating material. It would also be advantageous in these investigations to make use of carefully enclosed electrometers.

Activity Induced Outside the Influence of Radio-active Substances.

Attempts were made to produce induced radio-activity outside the action of radio-active bodies.

M. Villard subjected to the action of the cathode rays a piece of bismuth placed as anticathode in a Crookes tube; the bismuth was thus rendered active to a very slight degree, for it required an exposure of eight days to obtain a photographic impression.

Mr. MacLennan has exposed different salts to the action of cathode rays, afterwards warming them slightly. The salts then acquired the property of neutralising bodies positively charged.

Studies of this kind are of great interest. If, by using known physical agents, it were possible to create a considerable radio-activity in bodies originally inactive, we might hope thence to discover the cause of the spontaneous radio-activity of certain substances.

(To be continued).

ACTION OF PEROXIDE OF HYDROGEN AND HYPOCHLORITE OF SODIUM ON THE OXIDES OF THORIUM, ZIRCONIUM, AND CERIUM.

By L. PISSARJEVSKY.

By the action of a 30 per cent solution of peroxide of hydrogen on a concentrated solution of $Th(NO_3)_4$, a gelatinous, transparent precipitate of peroxide is formed; if the solution of peroxide of hydrogen is less concentrated, the precipitate takes some time to form. At the ordinary temperature the precipitate gives off oxygen, but at o it remains unchanged for a long time. It does not retain any NO_3H; dilute sulphuric acid decomposes it, and liberates peroxide of hydrogen; concentrated sulphuric acid gives off ozonised oxygen. The reaction of H_2O_2 on $Th(NO_3)_4$ is never complete; it is reversible, and may be expressed by the equation $Th(NO_3)_4+4H_2O_2=Th(O_2H)_4+4NO_3H$.

$Th(O_2H)_4$, which may be looked upon as the salt of the feeble monobasic acid, $H.O_2H$, becomes hydrolysed, giving:—

$$Th(O_2H)_4 + H_2O = Th(O_2H)_3OH + H_2O_2,$$
$$Th(O_2H)_4 + 2H_2O = Th(O_2H)_2(OH)_2 + 2H_2O_2.$$

$Th(O_2H)_2(OH)_2$, when washed on a filter, is also partially hydrolysed, and a peroxide is obtained in which the proportion of ThO_2 to active oxygen is as 1 : 1·35, instead of as 1 : 1·5, as required by the formula Th_2O_7, which has been attributed to peroxide of thorium; it is probable that the peroxide Th_2O_7 is simply a mixture of $Th(O_2H)_2(OH)_2$ and $Th(O_2H)(OH)_3$.

The reaction of peroxide of hydrogen on $Zr(NO_3)_4$ is analogous to the preceding reaction; we finally obtain $Zr(O_2H)(OH)_3$. The reaction of a 30 per cent solution of peroxide of hydrogen on a 17 per cent solution $Ce_2(SO_4)_3$ gives a gelatinous precipitate after about two hours which, when treated with sulphuric acid, gives off peroxide of hydrogen; sometimes there is a pulverulent precipitate mixed with it; this appears to be a compound of the peroxide and sulphuric acid.

The peroxides of Th, Zr, and Ce form with the same facility by the action of peroxide of hydrogen on the hydrated oxides, $M(OH)_4+H_2O_2=M(O_2H)(OH)_3+H_2O$.

The heats of neutralisation of $M(OH)_4$ by H_2O_2 are:—

For $Th(OH)_4$	+8·810 cals.
For $Ce(OH)_4$	+2·704 ,,
For $Zr(OH)_4$	+1·314 ,,

By the action of NaOCl on the oxides of Th and of Zr, we obtained the corresponding peroxides; with oxide of Ce we were able to prove the presence of peroxide in some experiments, but more often the results were negative, $Th(OH)_4+NaOCl=Th(O_2H)(OH)_3+NaCl$.

The formation of the peroxides of Th and Zr is effected best by passing an electric current through an alkaline solution of NaCl containing the oxides of Th or Zr in suspension in a state of continual agitation.

At the same temperature and with the same strength of current, the proportion of ThO_2 transformed into ThO_3 does not depend on the amount of $Th(OH)_4$ employed; the return of ThO_3 increases with the temperature (from 2° up to 45°) and with the strength of the current. No quantitative experiments have been made with $Zr(OH)_4$.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 483.

THE PIGMENTS OF GERANIUM AND OTHER PLANTS.

By A. B. GRIFFITHS, Ph.D., &c.

The pigments produced by bacteria are dependent upon the nature of the media as well as upon the specific peculiarities of the organisms. These fungi are remarkable for the enormous number chemical substances (pigments, ptomaïnes, &c.) elaborated during their activity.

The chemical composition of certain bacterial pigments have been ascertained. *Micrococcus prodigiosus* produces a pigment which has the formula $C_{38}H_{56}NO_5$ (Griffiths, *Comptes Rendus*, cxv., 32), and *Bacillus cyanogenus* produces a blue pigment, and I agree with Erdmann that this pigment is probably triphenylrosaniline. Pyocyanine ($C_{14}H_{14}N_2O$) is the blue pigment formed by *Bacillus pyocyaneus*. *Bacterium allii* (Griffiths, *Bulletins de l'Académie Royale de Belgique*, Series 3, xxiii., p. 268) produces a green pigment which is soluble in alcohol, Several of the bacterial pigments are fluorescent, and some give rise to phosphorescence.

The higher fungi also form a variety of pigments, and Zopf has investigated several of them. He has proved that many fungi contain one or several different lipochromes, and he considers that these substances function as reserves. In addition to the lipochromes, the higher fungi contain a large number of other pigments. Among these is the pigment ($C_{29}H_{20}O_{10}$) (Griffiths, *Comptes Rendus*, cxxx., p. 42) of *Amanita muscaria*, which contains no nitrogen in its molecule, and also the chromophyll of the geranium which is described in this paper.

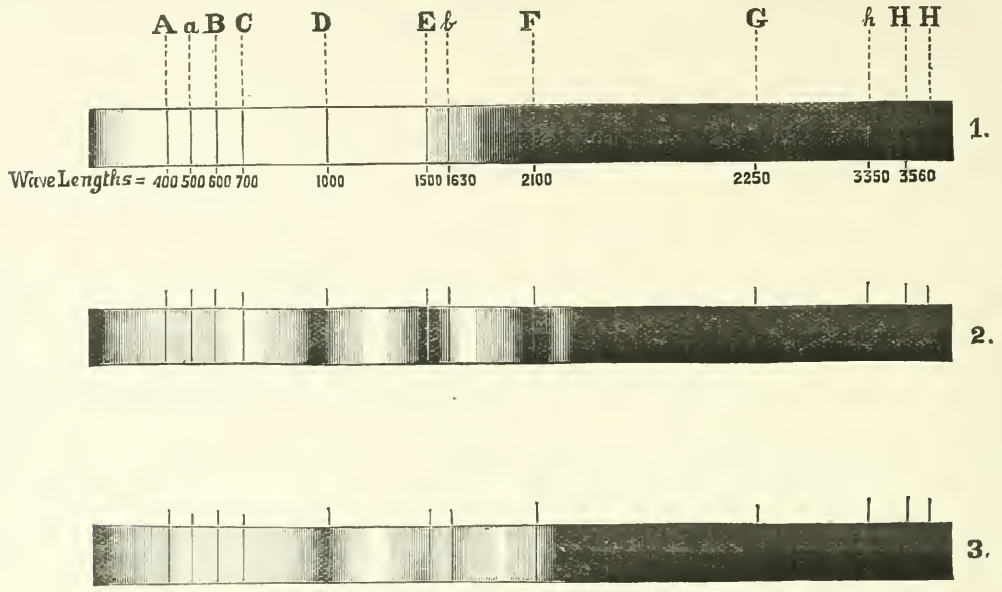
In Algæ there are a variety of pigments: chlorophylls, lipochromes, phycoerythrin, &c. Phycoerythin is probably a proteid, and according to Kerner and others may have a respiratory function.

The phanerogams contain chlorophylls (Gautier, "Chimie Biologique," p. 19; Etard, *Comptes Rendus*, cxx.), and many known and unknown pigments of great beauty. Among these pigments are two series, viz., the lipochromes and the anthocyans. The latter occur dissolved in the cell-sap, and vary in colour from blue to red. As a rule, these pigments are soluble in water (*e.g.*, the pigment of beet-root, &c.), and alkalis (NaOH, NH_4OH) change their colour from red to blue, and finally they become colourless. The chemistry and physics of the anthocyans have not been fully investigated, but it is more than probable that they are derivatives of tannic acid produced by oxidation. As tannic acid is generally looked upon as a waste product, it may be that the anthocyans belong to the same class of substances. Anthocyans are present in the petals of blue-bells, roses, and other flowers, and in such fruits as grapes, apples, &c. The great variation in the colours of anthocyans is due, in the first instance, to the chemical action of the living cell (*e.g.*, such actions as acidity, alkalinity, &c., account for much that occurs in the cells of plants). The living cell produces numerous anthocyans, all different in their chemical constitution, but still belonging to the same group or class of pigments.

The liprochromes vary from yellow to red, and are present in such fruits as tomatoes,* melons, &c., and in such flowers as daffodils, lilies, &c. It is probable that the different lipochromes of flowers and fruits have been formed from the pigments associated with chlorophyll.

The pigments to be described in this paper are crystalline substances possessing the characteristic colours of th flowers from which they came, and are odourless. Thes e

* According to Husemann (*Liebig's Ann.*, cxvii., p. 200) carrotin has the formula $C_{18}H_{24}O$.



SPECTRA OF FLOWER PIGMENTS.

1. Helianthus. 2. Geranium. 3. Verbena.

pigments may be preserved in sealed tubes, and when analysed they were found to contain carbon, hydrogen, oxygen, nitrogen, and sulphur. The pigment of geranium, however, contains no nitrogen or sulphur.

The flowers (petals) of geranium, helianthus, and verbena (red) were macerated in alcohol (90 per cent) for several hours, then heated, filtered, and finally the filtrate evaporated *in vacuo*. The pigments were treated with absolute alcohol, and the solution again evaporated *in vacuo*.

Each pigment has its characteristic absorption spectrum (see Fig.), the strength of the alcoholic solution in each case being 10 per cent and 1 c.m. thick.

The pigment of the geranium contains no nitrogen in its molecule, therefore it cannot be described as a proteid, although it may be derived from such a substance. An alcoholic solution of the red pigment evaporated to dryness yielded a crystalline substance, which was then submitted to chemical investigation.

0·2162 grm. of substance yielded 0·5006 grm. of CO_2 and 0·069 grm of H_2O.

	Found.	Calculated for $C_{15}H_{10}O_6$.
Carbon	62·85	62·93
Hydrogen ..	3·53	3·49
Oxygen	—	33·58

The red pigment has the formula $C_{15}H_{10}O_6$. The acetyl derivative, prepared by heating the pigment with 1 part of dry sodium acetate and 2 parts of acetic anhydride, crystallised from methyl alcohol in red needles. They melt at 125° C., and solidify on cooling without loss in weight.

The addition of potassium acetate to the boiling alcoholic solution of the pigment yielded orange coloured prisms, which were dried at 120° C. :—

0·5844 grm. yielded 0·1567 K_2SO_4 = K = 21·50 per cent.

$C_{15}H_{18}O_6K_2$ requires K = 21·54 per cent.

A diacetyl compound was obtained :—

1·2144 grm. yielded 0·7297 grm. $C_{15}H_{10}O_5 = C_{15}H_{10}O_6$ = 77·18 per cent.

$C_{15}H_8O_6(C_2H_3O)_2$ requires $C_{15}H_{10}O_6$ = 77·29 per cent.

220 grms. of flowers (petals) gave 2·8 grms. of pigment or 1·27 per cent.

The specific rotation of the alcoholic solution of the red pigment was ascertained to be—

$$[\alpha]_D = \frac{100 \times 3{\cdot}2}{2 \times 2{\cdot}13 \times 1{\cdot}002} = -74{\cdot}97°.$$

The chemical composition of the pigments of helianthus and verbena have not been ascertained, but they are nitrogenous substances. The specific rotations of their alcoholic solutions have been ascertained :—

Verbena—

$$[\alpha]_D = \frac{100 \times 4{\cdot}5}{2 \times 2{\cdot}6112 \times 1{\cdot}0032} = -85{\cdot}89°.$$

Helianthus—

$$[\alpha]_D = \frac{100 \times 3}{2 \times 2{\cdot}52 \times 1{\cdot}004} = -59{\cdot}28°.$$

The electrical resistances of selenium determined by the Wheatstone bridge method, and then exposed to alcoholic solutions of the pigments of helianthus, verbena, and geranium for fifteen minutes at a distance of 5 c.m., gave the following results :—

Pigments.	Resistances of selenium *before* exposure.	Resistances of selenium *after* exposure.
	Ohms.	Ohms.
Helianthus ..	420,000	415,000
Verbena	340,000	290,000
Geranium.. ..	462,000	320,000

As light, radium rays, and Röntgen rays produce a reduction of the resistance of selenium, these investigations appear to show that solutions of the pigments emit rays. Phosphorescence has been observed in many plants, and in some animals (*e.g.*, *Pyrophorus Noctilucus*); and Mr. T. A. Edison has proved that chlorophyll, curcumine (from turmeric), and daturine (from *Datura Stramonium*) give rise to phosphorescence.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extraordinary General Meeting, July 2, 1903.

Prof. Tilden, F.R.S., President, in the Chair.

The President stated that this meeting had been summoned to consider the following changes in the By-laws which had been proposed at one meeting of the Council, and considered and approved at a subsequent meeting.

It was proposed by the Treasurer, Dr. H. T. Brown, and seconded by Professor Thorpe,

"That By-law I., page 13, lines 3 and 4, be altered by *deleting* the words 'one year.'"

The By-law at present reads:—

". . . . ; and he shall be entitled, so long as his annual subscription be not one year in arrear, to one copy of the annual publica ions of the Society. . . ."

And that the Circulars in the Appendix be altered as follows:—

In Appendix No. 2, "Letter notifying the Election of a Member":—5th and 6th lines, p. 26, *delete* the words "the Assistant Secretary." After the words "before admission,*" *add* the words "Payment should be made direct to the Society's Bankers ( ) either by Cheque or Post-Office Order crossed a/c 'Chemical Society.' Your remittance should be accompanied by the enclosed Form with your Name and Address filled in."

In No. 3, "Annual Circular Letter of Treasurer":—*Delete* from "If paid" to end of circular, and *substitute* the same words as added in No. 2.

In No. 4, "Annual Circular Letter of the Treasurer to Fellows who are Two Years in Arrear of their Subscriptions":—*Delete* from "Payments should be made" to end of circular, and *substitute* the same words as added in No. 2.

The motion, having been submitted to the meeting, was declared by the President to have been carried unanimously.

The following are abstracts of papers received during the vacation, and published or passed for publication in the *Transactions*:—

112. "*The Composition of so-called Elæomargaric Acid.*" By T. Kametaka.

Maquenne having recently shown that the composition of Cloëz's elæomargaric acid is more closely expressed by $C_{18}H_{30}O_2$ than by the formula $C_{17}H_{30}O_2$ adopted by Cloëz, the author adduces evidence from his own work on the oil of *Elæococca vernicia* to show that the true formula for the acid is $C_{18}H_{32}O_2$. This proof depends on the formation of the bromine additive product, $C_{18}H_{32}O_2Br_4$, and on the result of the oxidation of the acid by permanganate, the product consisting of sativic acid, $C_{18}H_{32}(OH)_4O_2$, and a small amount of another hydroxy-acid, apparently dihydroxystearic acid. Titrations with standard caustic alkali and baryta solutions give, as a mean result, 280·5 for the molecular weight of elæomargaric acid, whilst $C_{18}H_{32}O_2$ requires 280.

113. "*Phosphoric Amidines.*" By R. M. Caven.

Phenyl-*p*-tolylphosphoric amidine,—

$$C_6H_5NH{\cdot}PO{:}N{\cdot}C_6H_4CH_3,$$

which is formed as a by-product in preparing anilino-*p*-toluidinophosphoryl chloride (*Trans.*, 1902, lxxxi., 1369), is identical with a compound obtained in the preparation of *p*-toluidinoanilinophosphoryl chloride, and which should accordingly have the formula $C_6H_4(CH_3){\cdot}NH{\cdot}PO{:}N{\cdot}C_6H_5$. This identity is not to be attributed to the mobility of a hydrogen atom (compare von Pechmann, *Ber.*, 1895, xxviii., 869 and 2362), but to the fact that the disubstituted phosphoryl chloride, in whichever way prepared, is one and the same substance, and that the derived amidine, whether a single substance or a mixture, results from the withdrawal of hydrogen chloride by the action of the substituting base.

Diphenylphosphoric amidine, $C_6H_5NH{\cdot}PO{:}NC_6H_5$, and di-*p*-tolylphosphoric amidine were prepared from dianilino- and di-*p*-toluidinophosphoryl chlorides respectively.

The formation of such amidines from the diarylaminophosphoryl chlorides by the elimination of hydrogen chloride is facilitated by the agency of basic oxides such as those of silver, mercury, and magnesium.

114. "*The Mechanism of Combustion.*" By H. E. Armstrong.

Assuming that chemical interchange and electrolysis are interchangeable equivalent terms, the author regards oxidation as an indirect process, inasmuch as the oxygen used is only indirectly incorporated with the oxidised matter; the oxidation takes place in a circuit composed of the oxidisable substance, conducting water, and oxygen; the last of these acting as the depolariser. The results obtained by Bone and Wheeler are discussed in the light of this hypothesis. It is contended that in the case of methane, for example, oxygen is introduced atom by atom, and that a substance such as carbon monoxide is a secondary product, not a direct product of oxidation nor of preferential oxidation of the carbon.

115. "*The Constituents of the Volatile Oil of the Bark of* Cinnamomum pedatinervium *of Fiji.*" By E. Goulding.

The bark of *Cinnamomum pedatinervium*, a tree indigenous to Fiji, on distillation with steam, yields nearly 1 per cent of a volatile oil which is almost colourless when first distilled, but gradually assumes a yellowish brown colour. This oil has a sweet aromatic odour, a pungent spicy taste, sp. gr. 0·964 at 15°/15°, $[\alpha]_D$ −4·96° and n_D 1·4963. Its chief constituents are:—(i.) A *terpene*, $C_{10}H_{16}$, which has a sp. gr. 0·8659 at 15°/15°, $[\alpha]_D$ −17·72°, and yields an uncrystallisable *dibromide*, $C_{10}H_{16}Br_2$; (ii.) linalool; (iii.) safrole; (iv.) eugenol; and probably (v.) eugenol methyl ether. The quantitative composition of the oil is approximately as follows:—Terpene, 15—20 per cent; alcohols, 30 per cent; esters, 1·5 per cent; safrole, 40—50 per cent; eugenol, 1 per cent; and 3 per cent of eugenol methyl ether (?).

116. "*Condensation of Phenols with Esters of Unsaturated Acids.*" Part VIII. By S. Ruhemann.

The compounds formed from α-naphthol and ethyl chlorofumarate must be formulated as derivatives of α-naphthaketocoumaran (compare *Trans.*, 1902, lxxxi., 419), because although guaiacol reacts with ethyl chlorofumarate to yield only ethyl guaiacoloxyfumarate, yet its isomeride, the monomethyl ether of resorcinol, condenses with the ester to furnish ethyl *m*-methoxyphenoxyfumarate and an orange-coloured ketocoumaran derivative, which is called *dimethoxybisbenzaronyl*.

The latter derivative has properties similar to those recorded for bisnaphtharonyl; both compounds are reduced to colourless ketocoumaran derivatives by zinc dust and acetic acid, these reduction products being readily oxidised and converted into red substances.

Ethyl phenylpropiolate, when condensed with the monomethyl ether of resorcinol, yields ethyl *m*-methoxy-β-phenoxycinnamate, the free acid of which loses carbon dioxide on heating and furnishes *m*-methoxyphenoxystyrene.

The diethyl ether of phloroglucinol reacts with ethyl chlorofumarate to form ethyl diethoxyphenoxyfumarate, and with ethyl phenylpropiolate to yield ethyl diethoxyphenoxycinnamate.

117. "*Action of Phosphorus Trichloride on the Aromatic Ethers of Glycerol.*" Part II. By D. R. Boyd.

The study of the action of phosphorus trichloride on glycerol diaryl ethers has been extended (*Trans.*, 1901,

lxxix., 1221), and the following substances have been prepared:—s-*Glycerol*, *di*-o-*tolyl ether* (*β-hydroxy-αγ-di*-o-*tolyloxypropane*) boiling at 226° under 13 m.m. pressure and melting at 36—37°; the corresponding meta-compound boiling at 232° (13 m.m.); *bisdi*-o-*tolyloxy*iso*propyl phosphite* and its para-*isomeride* which melt at 118—119° and 81—82° respectively; *di*-o- and *di*-m-*tolyloxy*iso*propylphosphorous acids* melting respectively at 88—89° and 85—87°, and certain of their metallic salts.

118. "*Attempts to Prepare Isomeric Quaternary Salts.*" By M. Barrowcliff and F. S. Kipping.

In view of the probable existence of isomeric salts of the type $\begin{matrix}R_1\\R_1\end{matrix}>NR_2R_3R_4$ (*Trans.*, 1903, lxxxiii., 873), the authors have investigated some compounds of this class, including certain salts of the ethyl-propylpiperidinium base already studied by Miss C. de Brereton Evans (*Trans.*, 1897, lxxi., 522); but although in all cases one of the radicles consisted of an optically active group, no indication whatever of the existence of isomerides has been observed.

Ethylpropylpiperidinium d-*bromocamphorsulphonate*, $C_5H_{10}NEtPr\cdot SO_3\cdot C_{10}H_{14}BrO$, crystallises in needles melting at 211°; it is very readily soluble in water and chloroform, sparingly so in ethyl acetate, and insoluble in ether and light petroleum. *Benzylmethylpiperidinium* d-*bromocamphorsulphonate*, $C_5H_{10}NMeBz\cdot SO_3\cdot C_{10}H_{14}BrO$, melts at 160° when anhydrous, and generally resembles the preceding compound. *Ethylpiperidine* d-*bromocamphorsulphonate*, $C_5H_{10}NEt,C_{10}H_{14}BrO\cdot SO_3H$, crystallises in needles melting at 158°.

These three salts, when repeatedly crystallised fractionally from various solvents under different conditions, did not yield dissimilar fractions. Molecular weight determinations made with ethylpropylpiperidinium iodide seem to show that whereas in aqueous solution the salt is ionically dissociated in a normal manner, yet in chloroform solution it is associated, possibly forming trimolecular complexes.

119. "*Some Salts of* d- *and* l-*α-Phenylethylamines.*" By A. E. Hunter and F. S. Kipping.

The authors have investigated several salts of the *d*- and *l*-components of *dl*-phenylethylamine in the hope of obtaining isomerides corresponding with those derived from hydrindamine, but without success.

When the d-*bromocamphorsulphonate* of the *dl*-base is fractionally crystallised from water, it affords a salt which separates in prisms melting at 206—207°, and having in aqueous solution a molecular rotation identical with that of the *d*-bromo-acid, namely, $[M]_D + 271°$; this salt, however, is not partially racemic, as might be inferred from its optical properties, but is the compound of the *l*-base; the salt of the *d*-base was not isolated.

Although the ion of the *l*-base appears to be devoid of optical activity, the free base is distinctly lævorotatory in aqueous alcoholic solution, its specific rotation being about $[\alpha]_D - 25°$; this behaviour is similar to that of the *d*- and *l*-hydrindamines.

The *benzoyl* derivative, prepared from *l-α*-phenylethylamine by the Schotten-Baumann method, melts at 120°, is optically inactive, and seems to be identical with that of the *dl*-base.

l-*α-Phenylethylamine* d-*chlorocamphorsulphonate* melts at about 198°, and has in aqueous solution a molecular rotation practically identical with that of the *d*-chloro-acid, namely, $[M]_D + 186°$.

l-*α-Phenylethylamine* d-*camphorsulphonate* melts at 149—150°, and is practically indistinguishable by polarimetric examination from the corresponding salt of the *dl*-base, both substances having a molecular rotation approximating very closely to that of the acid; apparently the salt of the *dl*-base is not a definite partially racemic substance.

120. "*β-Bromocinnamic Acids.*" By J. J. Sudborough and K. J. Thompson.

Small amounts of β-bromo*allo*cinnamic acid (m. p. 159—160°) are obtained by the action of alkalis on cinnamic acid dibromide, but are not produced when the ethyl ester is used instead of the free acid dibromide.

In aqueous solution, the products of the combination of hydrogen bromide and phenylpropiolic acids consist entirely of β-bromo- and β-bromo*allo*-cinnamic acids; the relative amounts of the two isomerides being but slightly affected by light, temperature, or concentration of the solvent. The nature of the combination is materially affected by the medium in which the hydrogen bromide is dissolved; when acetic acid is used, more of the β-bromo-acid and less of the β-bromo*allo*-acid are obtained than when saturated aqueous solutions are employed. With benzene and carbon disulphide, the chief product is *α*-bromo-cinnamic acid.

Similar results have been met with in the combination of ethyl phenylpropiolate and hydrogen bromide.

Under the influence of alkalis, β-bromocinnamic acid and its esters lose hydrogen bromide much more readily than the β-bromo*allo*-acid and its esters.

Attempts have been made to prepare Michael's *iso*-cinnamic acid in order to determine whether either the *allo*- or the *iso*-acid could be resolved into optically active constituents by the aid of active bases. The experiments made on the reduction of the β-bromo*allo*-acid indicate that the product, which consists of *allo*cinnamic acid with a trace of ordinary cinnamic acid, does not contain the *iso*-acid.

121. "*Vapour Pressure of Aqueous Ammonia Solution.*" Part II. By E. P. Perman.

The partial pressures of the ammonia and water-vapour evolved by an aqueous ammonia solution have been found by aspirating a known volume of air through the solution, and estimating the amounts of ammonia and water withdrawn. The experiments were made at temperatures ranging from 0° to 60°, and the concentration of the solutions employed varied from 0 to 22·5 per cent of ammonia.

It was found that the sum of the partial pressures was equal to the total pressure determined by the statical method, and also that the relationship between the partial pressures and the concentration of the solution is that deduced by Duhem and others for binary mixtures of liquids.

122. "*Isomeric Aminoamidines of the Naphthalene Series.*" (Fourth communication on Anhydro-bases). By R. Meldola, J. V. Eyre, and J. H. Lane.

The authors have succeeded in isolating the free base, ethenyltriaminonaphthalene, obtained by the reduction of dinitro-α-acetonaphthalide by tin and hydrochloric acid. The compound is characterised by its tendency to form complex hydrates containing 9½, 3½, or 1½ mols. of water. The *acetate*, $C_{12}H_{11}N_3,C_2H_4O_2,H_2O$, *oxalate*, $C_{12}H_{11}N_3,C_2H_2O_4,2H_2O$, and *mercurichloride*,—

$$C_{12}H_{11}N_3,HCl,HgCl_2,1\tfrac{1}{2}H_2O,$$

have been prepared.

The *N*-ethyl derivative of the acetyl derivative having the formula $C_{16}H_{17}ON_3,\frac{1}{2}H_2O$ has been obtained, and characterised by the formation of its *picrate*, $C_{16}H_{17}ON_3,C_6H_2(NO_2)_3OH,H_2O$, and *aurichloride*, $C_{16}H_{17}ON_3,HAuCl_4,2H_2O$.

By eliminating the NH_2 group in the ethenyltriaminonaphthalene by the diazo-method, an ethenyldiaminonaphthalene (methylnaphthimidazole) has been obtained, which differs from the only compound of this formula at present known (Prager, *Ber.*, 1885, xviii., 2161). The isomerism of the aminoamidines has thus been proved to extend to the parent compounds, so that the cause of the isomerism is to be sought in the structure of the amidine ring. The following salts and derivatives have been prepared:—*Hydrochloride*, $C_{12}H_{10}N_2,HCl,H_2O$, *chromate*, $C_{12}H_{10}N_2,H_2CrO_4,2H_2O$, and *picrate*.

The base itself has the formula $C_{12}H_{10}N_2,H_2O$, and the

water could not be expelled without decomposing the compound. The amidine ring apparently breaks down by the action of benzoyl chloride in presence of alkali with the formation of dibenzoyl-*o*-naphthylenediamine. The N-*methyl* derivative, an oily base, has a crystalline *picrate*, $C_{13}H_{12}N_2,C_6H_2(NO_2)_3OH$. The crystalline N-*ethyl* derivative, $C_{14}H_{14}N_2$, is anhydrous, and yields the following crystalline salts : — *Chromate*, $C_{14}H_{14}N_2,H_2CrO_4$, and *picrate*, $C_{14}H_{14}N_2,C_6H_2(NO_2)_3OH,H_2O$; its *aurichloride* contains $2H_2O$, and, when heated in the water-oven, becomes converted into the monohydrate. The *platinichloride* also yields hydrates containing 4, 2, and 1 mols. of water.

The *N*-ethyl derivative of the known ethenyldiaminonaphthalene (compare Otto Fischer, *Ber.*, 1901, xxxiv., 935) prepared for comparison with its isomeride, is found to be resinous, but the *chromate*, *picrate*, *platinichloride*, and *aurichloride* are well characterised.

The ethenyltriaminonaphthalene, obtained by the reduction of dinitro-α-acetonaphthalide by iron and hydrochloric acid (Markfeldt's base) yields a crystalline *oxalate* with $4H_2O$ and a *mercurichloride*, $C_{12}H_{11}N_3,2HCl,HgCl_2,5H_2O$. Its benzoyl derivative has now been prepared by the Schotten-Baumann method (compare *Trans.*, 1900, lxxvii., 1165).

Ethenyltriaminonaphthalene (Meldola and Streatfeild's base) is converted into its isomeride (Markfeldt's) by further reduction with iron and hydrochloric acid, but reduction with sodium amalgam in the presence of acetic acid does not bring about this transformation. Reduction of dinitro-α-acetonaphthalide with zinc and hydrochloric acid gives the original (M. and S.) base.

123. "*olythiosulphonic Acids of* p-*Diamines*." By A. G. Green and A. G. Perkin.

The series of polythiosulphonic acids of *p*-diamines formerly prepared by one of the authors in collaboration with A. Meyenberg (compare Eng. Pat. Specifications, 1898, Nos. 21832, 22460, 22847; 1899, Nos. 5039, 18658; and 1900, No. 4792) are well-crystallised compounds which, when oxidised together with primary amines and diamines, give rise to a series of black colouring matters possessing the characteristic properties of "sulphide" colours. The present communication deals with the further characterisation of these polythiosulphonic acids, especially of the di- and tetra-thiosulphonic acids of *p*-phenylenediamine, $C_6H_2(NH_2)_2(S{\cdot}SO_3H)_2$ and $C_6(NH_2)_2(S{\cdot}SO_3H)_4$, which are obtained by the oxidation of *p*-phenylenediamine in the presence of sodium thiosulphate, using 2 or 4 molecular proportions of the latter with a corresponding quantity of the oxidising agent.

Owing to the presence of the S_2O_3H groups in ortho-positions with respect to the amino-radicles, the *p*-phenylenediaminedithiosulphonic acid exhibits several characteristic condensations. Thus, with nitrous acid it gives a stable bisdiazosulphide,—

$$C_6H_2\left(\begin{array}{l}N_2\\|\\S\end{array}\right)_2;$$

with organic anhydrides or with aldehydes, it gives anhydro-compounds.

On boiling the di- or tetra-thiosulphonic acid with aqueous acids, sulphurous and sulphuric acids are eliminated, and yellow or red salts of sulphide bases are obtained. These bases, which appear to have the constitution—

$$C_6H_2(NH_2)_2\begin{array}{l}=S\\=S\end{array} \quad \text{and} \quad \begin{array}{l}S=\\S=\end{array}C_6(NH_2)_2\begin{array}{l}=S\\=S,\end{array}$$

are of dark colour, insoluble in water and other solvents, but dissolving in an aqueous solution of sodium sulphide, in which respect they resemble the "sulphide" colours; they are re-converted into the respective polythiosulphonic acids by prolonged treatment with sulphurous acid in the presence of air.

When treated with zinc dust, the dithiosulphonic acid is reduced to the disulphydride, $C_6H_2(NH_2)_2(SH)_2$.

124. "*The Rotation of the Menthyl Esters of the Isomeric Chlorobenzoic Acids*." By J. B. Cohen and S. H. C. Briggs.

The authors have prepared the menthyl esters of the mono- and di-chlorobenzoic acids, and have compared their specific and molecular rotations.

The following represents the order of optical activity, beginning with the least active :—2 : 6 ; 2 : 3 ; ortho ; 2 : 5 ; 2 : 4 ; 3 : 4 ; 3 : 5 ; unsubstituted ; meta ; para. These results lead to the following conclusions :—1. The greatest effect (decrease) in the rotation of the unsubstituted menthyl ester is produced when the halogen enters the ortho-position with respect to the carboxyl group ; the least, when the halogen is in the meta- and para-positions, which, singly, slightly increase the rotation. 2. The monohalogen derivatives accord with the rule laid down by Frankland and Wharton (*Trans.*, 1896, lxix., 1320, 1583), and confirmed by Guye and Babel (*Abstr.*, 1899, ii., 719), and Tschugaeff (*Abstr.*, 1903, ii., 2), and follow the order : ortho, unsubstituted, meta, para.

3. Two halogens attached to adjoining carbon atoms (2 : 3 and 3 : 4) produce a greater effect than either singly.

It might be expected that the rotations of the 2 : 3- and 2 : 5-esters would be approximately the same, inasmuch as the chlorine atoms in both isomerides occupy the ortho- and meta-positions with respect to the carboxyl group, but in reality the rotation of the 2 : 3-ester is much lower, and that of the 2 : 5-isomeride slightly higher than the value obtained for the ortho-compound.

The low rotation of the 3 : 4- and 3 : 5-esters does not support the theory of the lever-arm (Frankland and Wharton, *loc. cit.*).

125. "*The Reaction between Phosphorus and Oxygen*." Part I. By E. J. Russell.

A small quantity of water is necessary for the oxidation of phosphorus, and the reaction proceeds most rapidly when that amount is present which is left after drying with sulphuric acid. In the presence of much water-vapour, action is considerably retarded. The formation of ozone and hydrogen peroxide requires the presence of excess of water ; these bodies are not direct products of the reaction between phosphorus and oxygen.

Moderately dried phosphorus and oxygen react under all the pressures employed, and the phenomena of false equilibrium are not seen. The reaction may be divided into two stages :—In the first, oxidation is slow and accompanied by a very feeble glow, the action being apparently unimolecular ; the oxide formed is still under investigation. The second stage begins when the pressure falls below about 500 m.m. ; oxidation is continuously accelerated until all the oxygen is absorbed. The luminosity is very marked, and phosphorus pentoxide is formed. No simple expression could be found connecting the velocity of oxidation with the pressure of oxygen.

When an inert gas, such as nitrogen, is present, the phenomena are substantially the same, but the acceleration of the second period ceases after a time, and a retardation sets in. This variation is, however, explained on a purely mechanical hypothesis.

When phosphorus oxidises in moist oxygen, the reaction differs from that taking place in dry oxygen in the following respects :—

(*a*). It does not begin until the pressure of oxygen is less than about 500 m.m. ; when it does take place it is slower, and is much retarded during the earlier part of the reaction. The retardation is explained as being due to a protective film formed by the water on the phosphorus.

(*b*). Ozone and hydrogen peroxide are produced, and, in presence of nitrogen, these substances are accompanied by ammonium nitrite and nitrate. None of the theories at present held completely accounts for these observations.

If smaller quantities of water are present (4 or 5 m.m. pressure instead of 16 or 20 m.m.), the velocity curve does not differ greatly from that obtained in the absence of

water. And the difference observed when the higher quantity of water is present can readily be explained as being due to the protective layer of this liquid. There is no reason to suppose that the primary reaction between the phosphorus and oxygen differs in the two cases.

126. "*Action of Hydrogen Peroxide on Carbohydrates in the presence of Ferrous Sulphate.*" Part IV. By R. S. Morrell and J. M. Crofts.

The substances formed by adding hydrogen peroxide solutions of arabinose and rhamnose in the presence of ferrous sulphate yielded osazones with phenylhydrazine acetate, and it was therefore considered that arabinose and rhamnose had been oxidised to the corresponding osones (*Trans.*, 1889, lxxv., 786, and 1900, lxxvii., 1219). Aqueous solutions of these two osones have been found to react at the ordinary temperature with *p*-bromophenylhydrazine, giving rise to osazones. The action of larger quantities of hydrogen peroxide on glucose and fructose has been investigated, and the metallic salts of glyoxylic, glycollic, and trihydroxybutyric acids have been obtained. The formation of glycollic acid from glucose is peculiar, and is not easily accounted for on the assumption that the sugar molecule is transformed into an osone before a disruption of the carbon chain takes place.

127. "*Ethyl Benzylidencanilineacetoacctate.*" By R. S. Morrell and A. E. Bellars.

The authors find that the action of benzylideneaniline on ethyl acetoacetate gives rise to ethyl benzylideneanilineacetoacetate, which melts between 78° and 80° after recrystallisation from benzene and carbon tetrachloride. The addition of piperidine or minnte quantities of sodium ethoxide does not cause any change in the melting-point of the re-crystallised addition product (compare Schiff, *Ber.*, 1898, xxxi., 207; Rabe, *Ibid.*, 1902, xxxv., 3950; Francis, *Ibid.*, 1902, xxxv., 3949), but the solvents used in the recrystallisation must be pure, otherwise it is impossible to obtain the ethyl benzylideneanilineacetoacetate with a constant melting-point. The addition of small quantities of sodium ethoxide to a mixture of benzylideneaniline and ethyl acetoacetate causes the formation of a mixture of β_1- and β_2-forms of ethyl benzylidenediacetoacetate (Rabe, *Annalen*, 1900, 313, 176). The molecular weight of the ethyl benzylideneanilineacetoacetate in benzene or carbon tetrachloride solution decreases as the solution becomes more dilute, and also on heating or when it is kept for some time.

128. "*Studies on Enzyme Action. I. The Correlation of the Stereoisomeric α- and β-Glucosides with the Corresponding Glucoses.*" By E. F. Armstrong.

The stereoisomeric α- and β-alkyl glucosides have been converted, by means of enzymes, into the corresponding glucosides. It is thus shown that glucose has a lactonic structure, and consists, in solution, of a mixture of two stereoisomeric lactones. The changes in rotatory power which dissolved glucose undergoes involves the passage of one or other form of the lactone into a mixture of the two.

129. "*A Dynamical Study of the Friedel-Crafts Reaction.*" By B. D. Steele.

In order to determine, if possible, the mechanism of the Friedel-Crafts reaction, the synthesis of phenyl tolyl ketone from toluene and benzoyl chloride in presence of aluminium or ferric chloride, and that of phenyltolylmethane from toluene and benzyl chloride in presence of the same condensing agents, have been studied dynamically.

The course of the reaction in each case was followed by passing a rapid current of hydrogen through the reaction mixture, and titrating the hydrochloric acid thus carried over.

The following conclusions have been deduced:—

1. In the synthesis of a ketone from a hydrocarbon and an acid chloride in the presence of aluminium chloride, the explanation suggested by Perrier (*Ber.*, 1900, xxxiii., 815) and by Boeseken (*Rec. Trav. Chim.*, 1900, xix., 19; 1901, xx., 102) seems to be quite justifiable, providing that the aluminium chloride is not present in excess.

2. In the presence of an excess of the condensing agents, the reaction, instead of being unimolecular, becomes bimolecular, and is best explained by assuming that the reagents are two intermediate compounds, each containing aluminium chloride.

3. In the presence of ferric chloride, the reaction is also bimolecular, and is best explained on the foregoing assumption.

4. The synthesis of phenyltolylmethane from toluene and benzyl chloride, in the presence of either aluminium or ferric chloride, is a unimolecular reaction, due to the interaction of the toluene and a compound of the organic and metallic chlorides.

PHYSICAL SOCIETY.

Ordinary Meeting, November 13, 1903.

Dr. R. T. Glazebrook, F.R.S., President, in the Chair.

Sir Oliver J. Lodge read a paper on "*Means for Electrifying the Atmosphere on a Large Scale.*"

Twenty years ago the author was engaged with Mr. J. W. Clarke on an investigation of the dark spaces seen near hot bodies placed in illuminated smoke. The existence of these dust-free spaces was discovered by Tyndall, and the phenomenon had been investigated by Lord Rayleigh. Tyndall worked with high temperatures, and attributed the effect to the burning of the dust near the hot body. Such, however, cannot be the case, as the spaces exist when inorganic dust, such as oxide of magnesium, is used. The conclusion at which Messrs. Lodge and Clark arrived (see *Phil. Mag.*, 1884) was that the result was due to an aërial bombardment from the hot wire which drove the particles away, and they tried the effect of electrifying the hot body to see if there was any modification of the dark space. A new phenomenon was discovered; the whole of the dust being driven to the sides of the containing vessel. This experiment was shown by the author at the British Association meeting in Montreal in 1884, and subsequently, on a larger scale, at the Royal Institution. In the latter experiment two pieces of wire gauze, connected to the terminals of an electric machine, were placed opposite each other in a smoke-filled chamber, through which a current of smoke was slowly passing. Upon electrifying the plates the smoke ceased passing, the dust particles cohered, hovered in the air, and were either driven to the sides of the chamber or fell to the bottom. In the case of mist, electrification of steam in a bell-jar converted it into fine rain. It seems therefore possible that rain might be produced by the electrification of a cloud. Sir Oliver Lodge has tried at Liverpool to disperse fogs by discharging electricity into them. For this purpose a large mast was erected on the roof of the University College buildings. It terminated in a bundle of points, to which electricity was conveyed from a Wimshurst machine by a wire supported by specially constructed insulators. In order to drive electricity from a point far removed from a surface a high potential is necessary, and sometimes a large gas flame was used to supplement the points. Upon one occasion the discharge of electricity from the flame was sufficient to keep a clear space of 50 or 60 yards radius in a dense fog. The author had hoped to induce the Mersey Dock Board to try the principle on a large scale, having a series of positive discharges on one side of the river and a series of negative discharges on the other; but he felt a certain reluctance in recommending the method to practical men so long as it was necessary to derive the current from a Wimshurst machine. A dynamo would be a more suitable generator if it were possible to get a sufficiently high potential. The way out of the difficulty is to rectify a high-tension alternating current, and Sir Oliver Lodge has for some time been considering the possibility of doing this by utilising Cooper-Hewitt mercury

lamps. A study of these lamps has led him to believe that their rectifying power is much assisted by the outside metallic coating which surrounds the mercury electrode, and which is connected to the positive terminal of the lamp. In order to rectify an alternating discharge, four lamps are so arranged in the form of a quadrilateral that, when the leads from the terminals of an alternating transformer are connected to two opposite corners, two unidirectional currents are obtained from the other corners. Experiments have been made at Birmingham by sending the current from a high-frequency alternator (3000 $\frown\!\smile$ *per sec.*) through the primary of an induction coil and connecting the terminals of the secondary to the rectifiers. The length of the rectified spark can be increased by putting a number of lamps in series in each arm of the quadrilateral arrangement. Sir Oliver Lodge performed an experiment at the meeting to show the dissipation of fog by electrification. The current from an alternator was passed through the primary of a coil and the terminals of the secondary connected to the rectifiers, twelve lamps in all, three in series in each arm. This arrangement is capable of giving a rectified spark 2 or 3 inches long, the unidirectional nature of which can be proved by passing it through a Crookes or a Röntgen tube. Some magnesium wire having been burnt under a large bell-jar to fill it with a cloud of magnesium oxide, the jar was then illuminated by the light from an electric lamp. Passing through the base-piece upon which the bell-jar was placed was a conductor which terminated in a point inside the jar. When the terminals between which the rectified discharge was passing were separated and the other end of this conductor was joined to one of them, the electricity streaming from the point into the clouded atmosphere caused an immediate deposition of the magnesium oxide.

Prof. W. E. AYRTON congratulated the author, and expressed his interest in the experiment showing the deposition of magnesium oxide. He pointed out that the combination of four Nodon valves for obtaining a continuous current from an alternating one had been used before. Dealing with the rectifier itself, he said his feeling was that the rectification was due to a difference in the electrodes and not to any special proximity of two electrodes through the glass as suggested by Sir Oliver Lodge. There were many cases of rectification—a metal-carbon arc for instance. In this case the explanation of the phenomenon was probably connected with the fact that one electrode was metallic and the other carbon. In the mercury lamp both electrodes were metallic, but the metals were very different from each other. Prof. Ayrton said that Prof. Steinmetz had recently shown him some interesting experiments with mercury arc-lamps resembling in some details the Cooper-Hewitt lamp. There was, however, no choking coil, the starting being effected by an electro-magnet capable of separating two tags within the tube, and causing a small arc which started the lamp. There was also no branch lead from the positive electrode to the mercury end of the lamp. In his opinion this connection was only a starting device in the Cooper-Hewitt lamp. Prof. Ayrton concluded by expressing his pleasure that the administrative duties of Sir Oliver Lodge had not interfered with his keen interest in scientific research.

Prof. H. L. CALLENDAR expressed his interest in the paper and in the experiments shown. In connection with the rectification he pointed out that under certain conditions any vacuum-tube would act as a rectifier, illustrating the point by an experiment with an X-ray tube. The phenomenon was noticed by Hittorf thirty years ago, and attributed by him to the constriction around the negative electrode.

Mr. W. DUDDELL said he should like to discuss the rectifying power of mercury lamps. Any two different electrodes in air will rectify to some extent. In the case of two carbons, the diameters of which are as two to one, the resistance between them varies by 5 or 6 per cent, according as the current is passed one way or the other. With a metal-carbon arc it is possible to stop the current altogether. A point and plate will also act as a rectifier. He thought that the condenser arrangement was to facilitate starting, and expressed the opinion that the rectification was due to the temperature of the electrodes and the temperature gradients near them. The temperatures of the mercury and iron in a mercury lamp were very different, and in the case of a point and plane there was a difference of temperature because of the cooling of the plane by radiation. He had also found that the best rectification takes place between electrodes having a high potential difference, and that when using the lamp for practical purposes the presence of impurities improved it by facilitating starting.

Dr. C. CHREE pointed out that there was a potential gradient in the atmosphere from the ground upwards which sometimes amounted to 1000 volts per metre, and was often 150 volts per metre. He asked if this difference of potential between the ground and the tops of high trees would have any effect upon the dissipation of fog.

Sir OLIVER LODGE, replying to Dr. Chree, said it had occurred to him that atmospheric electricity must be taken into account, and said it was quite feasible that point discharges from trees might have some effect upon fogs, but not enough. Replying to Mr. Duddell, he said they had found that for high tension rectification it was necessary to have as good a vacuum as possible, but for lamps working on low voltages it was beneficial to permit a residue of impurities. He said he was still of the opinion that the outside connection assisted the rectification in some tubes by throwing a great strain on the gas near the cathode.

Sir OLIVER LODGE then described an Arrangement for Driving Mercury Pumps, designed by himself and Mr. B. Davies.

The apparatus was constructed because the work necessary to make large numbers of vacuum-tubes renders it essential to drive the pump hydraulically. The preliminary exhaustion is effected with an ordinary Fleuss pump and the work completed by using a Töpler mercury pump. The reservoir of the pump is suspended from the rim of a six-inch wheel, and is almost counterbalanced by a water-vessel suspended from the rim of a two-foot wheel fixed upon the same axle. The water-vessel is capable of moving up and down between vertical guides, and mechanism is so arranged that when it reaches the top of the guides a tap is turned, and it is filled with water. The increase in weight causes it to descend and raises the pump reservoir. When it reaches the bottom of the guides a valve in the bottom of the vessel is opened automatically and the water is discharged. The vessel then rises again, and the process is repeated. Keyed to the axle carrying the two wheels referred to, there is a third wheel, one foot in diameter, over the rim of which passes a friction band. The function of this arrangement is to control the upward and downward motion of the water-vessel, bringing it to rest quietly at each end of the journey, and yet allowing it to move quickly. There is also a device at the bottom of the guides for keeping the valve of the vessel open until the whole of the water has been discharged. The mercury which overflows from the pump is conducted back to the reservoir, thus giving a circulation of mercury and automatically replenishing the reservoir.

Reaction between Benzene and Cellulose.—A. M. Nastukof.—The author has already obtained a product of the reaction between benzene and cellulose; this product appears to be a tetraphenylised derivative of cellulose. Analysis shows the presence of sulphur; the best method of representing the results would be to consider this compound as a tetraphenylcellulose containing $2SO_2$ for $6[C_6H_6O_5(C_6H_5)_4]$, and which, dried in the desiccator, has lost $9H_2O$, or which has lost $12H_2O$ when dried at 105—110°; according to the method adopted we get the formula $C_{180}H_{134}O_{25}S_2$ or $C_{180}H_{128}O_{22}S_2$. From the analyses of the products of oxidation and dry distillation, it must be admitted that the groups C_6H_5 replace the H's fixed directly to the C's, and not the H's of the OH groups.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 505.

NOTICES OF BOOKS

Introduction to Metallurgical Chemistry, for Technical Students. By J. H. STANSBIE, B.Sc. (Lond.), F.I.C., &c. With 46 Illustrations. Bristol: John Wright and Co. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. 1903. Pp. 200.

As a preparatory course to the study of metallurgy proper, we are glad to recommend the book now before us. It deals principally with the chemistry of the metals, though of course a certain amount of space is devoted to the other elements. Metallurgy, in the ordinary sense of the term, deals almost entirely with operations requiring the use of fire, but it is of the greatest importance that students should be well acquainted with the chemistry of the elements dealt with in metallurgical operations, and in these days of technical education and specialism such a book as the present one will be found of great assistance to those students who have decided on making metallurgy their special study.

The book is divided into twenty-five chapters, the earlier ones being devoted to the general physical and chemical properties of the elements, both metallic and non-metallic. In Chapter X. we come to what may be considered the more technical side of the subject, viz., carbon and its compounds. This chapter is followed by those on "Reduction," "Combustion," "Silicon, and its Compounds with Oxygen and Metals," &c.

Electro-chemical action also finds a place, and students would do well to pay close attention to this branch of the subject, as electricity is becoming daily more and more closely associated with metallurgical operations.

The book is well arranged and the descriptions clear, and there are a number of questions at the end of each chapter on the subjects just dealt with; we must, however, again point out a fault which is too common in books of this class, viz., the character of the illustrations. Many of them are entirely superfluous, as they illustrate simple bits of apparatus which must of necessity already be familiar to any intelligent youth who has taken any interest in chemistry or science. The book closes with an appendix and a short index of three pages.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

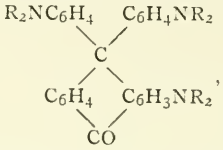
NOTE.—All degrees of temperature are Centigrade unless otherwis expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 16, October 19, 1903.

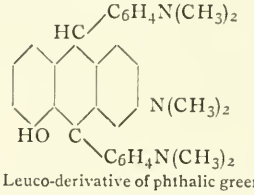
Carbon Vapour.—M. Berthelot.—It is known that incandescent electric lamps contain a filament of amorphous carbon, obtained by calcination of vegetable matter. This thread is raised to a red heat in a vacuum by the electric current, and gives forth a trace of carbon vapour, which condenses on the bulb, forming, after a time, a brown deposit. The author investigates the state of this carbon vapourised at the lowest possible temperature, and compares it with the known allotropic forms of carbon. The result of his experiments is that the carbon vapour obtained under these conditions, *i.e.*, at the lowest possible temperature, contains no graphite and no diamond, but only a variety of amorphous carbon. He also makes some experiments on the vapour-tension of carbon.

Estimation of Argon in Atmospheric Air.—Henri Moissan.—Already noticed.

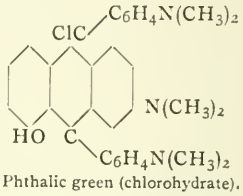
Products of Condensation of Tetramethyldiamidophenyloxanthranol with Benzene, Toluene, and Dimethylaniline: Phthalic Green.—A. Haller and A. Guyot.—The addition products of tetramethyldiamidophenyloxanthranol with benzene, toluene, and dimethylaniline are not amidodiphenylanthrones, the two tetraalcoyldiamidodiphenylanthrones which the authors have described in a previous paper, and whose constitution,—



is not doubtful, are yellow in the free state, give with acids colourless salts, and do not combine with hydroxylamine or phenylhydrazine; whilst the former substances are colourless in the free state, forming with acids strongly coloured salts and combining with phenylhydrazine and hydroxylamine with loss of 2 mols. of water. A series of experiments on their constitution lead to the conclusion that they have the following formulæ:—

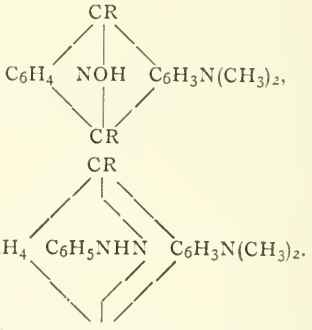


Leuco-derivative of phthalic green.



Phthalic green (chlorohydrate).

The combination of the bases with hydroxylamine and phenylhydrazine may be regarded in the following manner:—



R representing the radicles C_6H_5, $C_6H_4CH_3$ and $C_6H_4N(CH_3)_2$.

Composition of Zinc Peroxide.—M. Kuriloff.—The zinc oxides prepared by M. de Forcrand show forms of intermediate oxidation, and their composition depends on the methods used to obtain them. The composition of zinc peroxide is analogous to cadmium peroxide and corresponds to the formula $Mo_2M(OH)_2$. The author asserts that this latter formula is the only one definitely established up to the present time, the other types not having been verified. After establishing the individuality of the different degrees of oxidation, it will be possible to definitely settle the question as to the characteristics of these peroxides and compare them with the peroxides of barium, strontium, and calcium.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. A. K. Huntingdon, Sir Oliver Lodge, LL.D., D.Sc., F.R.S., J. Francis Mason, and Edward H. Woods were elected members.

Action of Binoxide of Sodium on Paraldehyde.—L. Vanino.—Binoxide of sodium in the form of powder, mixed with paraldehyde, oxidises it rapidly, and bursts into flame. Contrary to most of the oxidising reactions of this body, this latter one takes place by simple contact, without previous heating or the addition of water. Formic aldehyde in aqueous solution generally detonates under the influence of peroxide of sodium.—*Zeit. Anal. Chem.*, vol. xli., p. 619.

Approximate Estimation of Albuminoids.—A. Jolles.—Permanganate of potassium in slightly acid solution oxidises albuminoids. The amount of nitrogen given off by hypobromite of soda in the neutralised liquor is nearly a constant fraction of the original albuminoid. This method can be applied to the estimation of albuminoids in urine in the following manner:—Precipitate 25 or 50 c.c. of urine, at boiling temperature, by means of acetic acid in the presence of chloride of sodium. The precipitate being collected in a beaker with 300 to 400 c.c. of water, add 5 c.c. of sulphuric acid ($d = 1{\cdot}4$), and boil while gradually adding permanganate up to 8 grms. per litre, until the precipitate of peroxide is constant. Dissolve the latter in oxalic acid, and concentrate to 50 c.c. Neutralise when cold with soda, then set free the nitrogen in a ureometer. The weight of nitrogen, multiplied by 7·68, represents the weight of albuminoid. The error found by comparison with the gravimetric method is about 2·5 per cent more or less.—*Zeit. Anal. Chem.*, vol. xli., p. 589.

Use of Sulphate of Hydrazine in Analysis.—E. Orlof.—Sulphate of hydrazine, while exercising its oxidising function in alkaline solution, gives off a volume of nitrogen equal to the volume of oxygen reacting: $SO_4N_2H_4H_2 + O_2 = SO_4H_2 + 2H_2O + N_2$. The author has made use of this reaction for analysis by oxidation in alkaline solution. The oxidising agent is first titrated with respect to the N given off with $SO_4N_2H_4H_2$. The substance is treated with the titrated solution of the oxidiser, and, when the reaction is terminated, $SO_4N_2H_4H_2$ is added; the number of c.c. of nitrogen given off represents the volume of oxygen not used in oxidising the substance in question. The author has used this method in the following oxidising reactions:—1. Oxidation by means of ferricyanide and KOH according to the equation $2K_3FeCy_6 + 2KOH = 2K_4FeCy_6 + H_2O + O$. 2. Oxidation by means of $KMnO_4$ in alkaline solution: $6KMnO_4 = 3K_2O + 2Mn_3O_4 + 13O$. 3. Oxidation by means of chloride of lime, and, in general, by means of chlorine, bromine, and iodine in alkaline solution. The methods, which will be destribed in detail in a future paper, are applicable to the analysis of various industrial products.—*Journ. Soc. Phys Chim. R.*, vol. xxxiv., p. 449.

Synthesis of a New Aromatic Hydrocarbide Decacyclene (Trinaphthylenebenzene), and of a Derivative of Thiophene having a Red Colour, Dinaphthylenethiophene.—C. Dziewonski.—100 grms of acenaphthene and 23 grms. of finely powdered sulphur were thoroughly mixed and heated gently in a half litre flask. A strong reaction takes place at about 205° with the evolution of sulphuretted hydrogen, and the melted mass gradually takes a deep red colour. Towards the end of the reaction, which is known by the diminution of the volume of sulphuretted hydrogen given off, the temperature is raised to 290—294° for a few minutes. When the reaction has become less at this temperature, which must not be exceeded, however, or there would be danger of decomposition, the whole is allowed to cool, and is treated with boiling alcohol five or six times in the endeavour to remove all the acenaphthene which has not entered into the reaction. The substance remaining is extracted with benzene, and on evaporating the latter a red body is obtained which is crystallised, mixed with animal-black, several times in toluene; in this manner a pure substance is obtained in very fine red needles. A further quantity of this red body can be extracted from the residue in the flask by treating it with toluene. Finally, the residue, mixed with animal-black, is treated with boiling cumol, which dissolves a certain proportion; this eventually crystallises out in the form of small golden-yellow needles. The author then describes a number of the reactions of these bodies.—*Bull. Soc. Chim.*, vol. xxix., No. 9.

MEETINGS FOR THE WEEK.

Monday, 23rd.—Society of Arts, 8. (Cantor Lectures). "The Mining of Non-Metallic Minerals," by Bennett H. Brough.

Wednesday, 25th.—Society of Arts, 8. "The Universal Exposition at St. Louis, U.S.A., 1904," by George F. Parker.

Friday, 27th.—Physical, 8. (At the Royal College of Science, South Kensington). "An Electrical Thermostat," by S. Darwin. "Occurrence of Cavitation in Lubrication," by S. Skioner. "Lecture Experiment in Electrical Resonance," by Dr. W. Watson.

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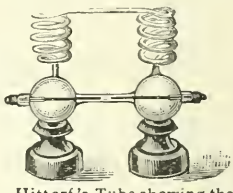

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2296.

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Continued from p. 249).

Chapter IV. (*continued*).

Variations of Activity of Radio-active Bodies. Effects of Solution.

The activity of polonium, as I have said above, diminishes with time. This diminution is slow, and does not take place at the same rate with different specimens. A sample of bismuth-polonium nitrate lost half its activity in eleven months, and 95 per cent in thirty-three months. Other specimens have evidenced similar diminution.

A specimen of metallic bismuth containing polonium was prepared from the nitrite, its activity after preparation being 100,000 times that of uranium. The metal is now only a body of medium radio-activity (2000 times that of uranium). Its radio-activity is determined at intervals. In six months it has lost 67 per cent of its activity.

The loss of activity does not seem to be facilitated by chemical action. In rapid chemical changes no considerable loss of activity has in general taken place.

In contrast to that which occurs with polonium, radium salts possess a permanent radio-activity which evidences no appreciable diminution after many years.

A freshly prepared radium salt in the solid state does not at first possess an activity of constant strength. Its activity increases from the time of preparation until it attains a practically constant limiting value after about one month. The opposite is the case for a solution. When freshly prepared the solution is very active, but when left exposed to the air it rapidly loses activity, and finally reaches a limiting activity which may be considerably less than the original. These variations of activity were first observed by M. Giesel. They are easily accounted for by the emanation theory. The diminution of the activity of the solution corresponds to the loss of the emanation which escapes into space; this diminution is much less when the solution is contained in a sealed tube. A solution which has lost its activity in air recovers a greater activity in a sealed tube. The time of increase of the activity of the salt which, after solution, has been recently obtained in the solid state, is that during which the emanation is being newly stored in the solid radium.

The following are some experiments on this subject :—

A solution of barium-radium chloride left exposed to the air for two days becomes 300 times less active.

A solution is enclosed in a stoppered vessel; the vessel is opened, the solution poured into a dish, and the activity determined :—

Activity immediately determined	67
,, after two hours	20
,, ,, two days	0·25

A solution of barium-radium chloride, which has been kept open to the air, is enclosed in a sealed glass tube, and the radiation of this tube determined. The following results were observed :—

Activity determined immediately	27
,, ,, after 2 days..	61
,, ,, ,, 3 ,, ...	70
,, ,, ,, 4 ,, ...	81
,, ,, ,, 7 ,, ...	100
,, ,, ,, 11 ,, ...	100

* Thesis presented to the Faculté des Sciences de Paris.

The initial activity of a solid salt after preparation is feeble in proportion as the time of solution was long. A greater proportion of activity is then transmitted to the solvent. The following figures give the initial activity with a chloride whose limiting activity is 800, and which was kept for a given time in solution; the salt was afterwards dried, and its activity immediately determined :—

Limiting activity	800
Initial activity after solution and immediate evaporation	440
Initial activity after the salt has remained dissolved 5 days	120
Initial activity after the salt has remained dissolved 18 days..	130
Initial activity after the salt has remained dissolved 32 days..	114

During this experiment the dissolved salt was placed in a vessel merely covered with a watch-glass.

I made with the same salt two solutions which I kept in sealed tubes for thirteen months; one of these solutions was eight times the strength of the other :—

Initial activity of the salt in concentrated solution after evaporation	200
Initial activity of the salt in dilute solution after evaporation..	100

The loss of activity of the salt is therefore greater when the amount of solvent is greater, the radio-active energy transmitted to the liquid having a greater volume of liquid to saturate and a greater space to fill. The two specimens of the same salt, which thus had a different initial activity, further increased in activity at very different rates at first; at the end of one day they had the same activity, and the increase of activity now continued in the same manner for both till the limit was reached.

When the solution is dilute, the loss of activity by the salt is very rapid, as is shown by the following experiments :—Three equal portions of the same radium salt are dissolved in equal quantities of water. The first solution (*a*) is allowed to stand in contact with the air for one hour, and is then evaporated. The second solution (*b*) has a current of air passed through it for one hour, and is then evaporated. The third solution (*c*) is left exposed to the air for thirteen days, and then evaporated to dryness. The initial activity of each of the three salts is :—

For portion *a*	145·2
,, *b*	141·6
,, *c*	102·6

The limiting activity of the same salt is about 470. We thus see that the greatest part of the effect was produced at the end of one hour. Further, the air current bubbling through solution *b* for one hour produced little effect. The proportion of salt in solution was about 0·5 per cent.

Radio-active energy in the form of an emanation is propagated with difficulty from solid radium in air; it experiences the same resistance to propagation from solid radium in a liquid. When radium sulphate is shaken with water for a whole day, its activity after the operation is practically the same as that of a portion of the same sulphate left exposed to air.

On placing the radium salt in a vacuum, all the emanation capable of displacement is withdrawn. However, the radio-activity of a radium chloride kept *in vacuo* for six days was not sensibly affected by the operation. This experiment shows that the radio-activity of the salt is principally due to the radio-active energy generated within the particles, and which is unaffected by the vacuum.

The loss of activity that radium undergoes when in solution is relatively greater for the penetrating rays than for the absorbable rays. The following are examples of this :—

A radium chloride which had reached its limit of activity, 470, was dissolved and left in solution for one hour; it was then evaporated, and its initial radio-activity determined by the electrical method. The total initial radiation was

found to be equal to the fraction 0·3 of the total limiting radiation. If the determination of the intensity of radiation be made by covering the active body with an aluminium screen 0·01 m.m. thick, the initial radiation which traverses this screen is found to be only the fraction 0·17 of the limiting radiation traversing the same screen.

When the salt has been thirteen days in solution, the total initial radiation is found to be the fraction 0·22 of the total limiting radiation, and is 0·13 of the limiting radiation after traversing 0·01 m.m. of aluminium.

In the two cases the ratio of the initial radiation after solution to the limiting radiation is 1·7 times as great for the total radiation as for the radiation which has traversed 0·01 m.m. of aluminium.

It must further be mentioned that on evaporating the product after solution, it is impossible to avoid a certain period of time during which the product is in an intermediate condition, neither entirely solid nor entirely liquid. Neither can one avoid warming the product to remove the water quickly.

For these two reasons it is scarcely possible to determine the true initial activity of the product passing from solution to the solid state. In the experiments just quoted, equal quantities of the active bodies were dissolved in the same quantity of water, and the solutions were then evaporated to dryness under conditions as identical as possible, and without heating above 120° or 130°.

I investigated the law according to which the activity of a solid radium salt increases, from the moment in which the salt is obtained dry after solution to the moment in which it reaches its limit of activity. In the tables which follow, the intensity of radiation, I, is represented as a function of the time, the limiting intensity being supposed equal to 100, and the time being reckoned from the moment at which the product was dried. Table I. (Fig. 12, Curve I.) refers to the total radiation. Table II. (Fig. 12, Curve II.) refers only to the penetrating rays (rays which have traversed 3 c.m. of air and 0·01 m.m. of aluminium).

Table I.

Time. Days.	I.
0	21
1	25
3	44
5	60
10	78
19	93
33	100
67	100

Table II.

Time. Days.	I.
0	1·3
1	19
3	43
6	60
15	70
23	86
46	94

I made several other series of determinations of the same kind, but they do not absolutely agree with one another, although the general character of the curves obtained remains the same. It is difficult to obtain very regular results. It may, however, be remarked that the acquisition of activity requires more than one month for its production, and that the most penetrating rays are the most deeply affected by solution.

The initial intensity of the radiation which is able to traverse 3 c.m. of air and 0·01 m.m. of aluminium is only 1 per cent of the limiting intensity, whilst the initial intensity of the total radiation is 21 per cent of the total limiting radiation.

A radium salt which has been dissolved and recently evaporated to dryness possesses the same power of causing induced activity (and, consequently, of allowing the escape of an emanation), as a specimen of the same salt which, after having been prepared in the solid state, has remained in this condition long enough to have attained its limiting radio-activity. The radiant activity of these two products is, however, quite different; the former is, for example, five times less active than the latter.

Variations of the Activity of Radium Salts on Heating.

When a radium compound is heated, it gives off an emanation and loses activity. The more intense and the more prolonged the heating, the greater is the loss of activity. Thus, on heating a radium salt for one hour to 130°, it loses 10 per cent of its total radiation; on the other hand, heating for ten minutes to 400° produces no apparent effect. Heating to redness for several hours destroys 77 per cent of the total radiation.

The loss of activity on heating is more considerable for the penetrating than for the absorbable rays. Thus, heating for several hours destroys about 77 per cent of the total radiation, but the same amount of heating destroys nearly the whole (99 per cent) of the radiation that traverses 3 c.m. of air and 0·01 m.m. of aluminium. If barium-radium chloride be kept fused for several hours (towards 800°) 98 per cent of the radiation capable of traversing 0·3 m.m. of aluminium is destroyed. The penetrating rays may be considered as no longer in existence after intense and prolonged heating.

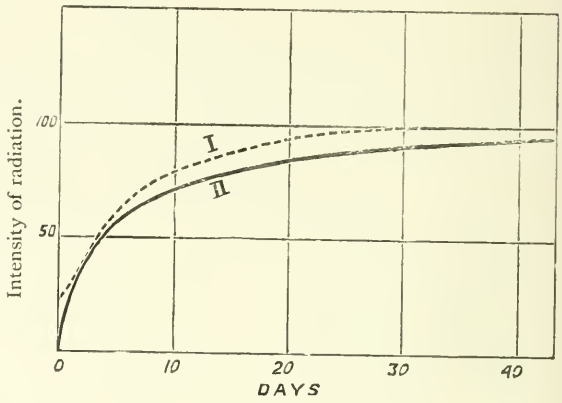


Fig. 12.

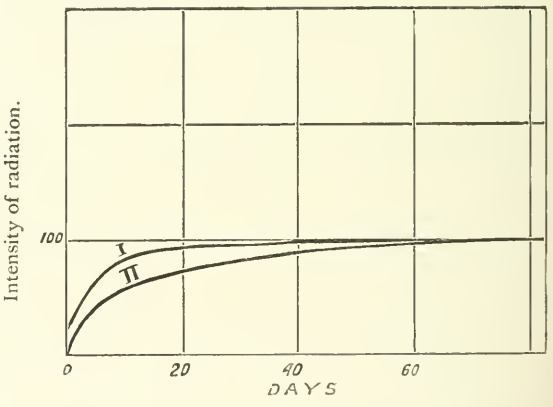


Fig. 13.

When a radium salt has lost part of its activity by heating, the diminution is not lasting; the activity of the salt is spontaneously regenerated at the ordinary temperature, and approaches a certain limiting value. I have observed the curious fact that this limit is higher than the limiting activity of the salt before being heated—this, at least, is the case with the chloride. I give examples of this:—A specimen of barium-radium chloride which, after having been prepared in the solid state, has long since attained its limiting activity, possesses a total radiation represented by the number 470, and a radiation capable of traversing 0·01 m.m. of aluminium, represented by the number 157. This specimen is heated to redness for several hours. Two months after the heating it attains its limit of activity with a total radiation equal to 690, and a

radiation through 0·01 m.m. of aluminium, equal to 227. The total radiation and the radiation transmitted by aluminium are therefore increased respectively in the ratios $\frac{690}{470}$ and $\frac{227}{156}$. These two ratios are practically equal to one another, and are equivalent to 1·45.

A specimen of radium-barium chloride which, after having been prepared in the solid state, has attained a limiting activity of 62, is maintained in a state of fusion for some hours; the fused product is then powdered. The product regains a new limiting activity equal to 140, which is twice as great as that to which it was able to attain when prepared in the solid state without having been sensibly heated during evaporation.

I have investigated the law of increase of activity of radium compounds after heating. The following are the results of two series of determinations:—The figures of Tables I. and II. represent the intensity of the radiation (I) as a function of time, the limiting intensity being supposed equal to 100, and the time being reckoned from the close of the heating. Table I. (Fig. 13, Curve I.) refers to the total radiation of a specimen of barium-radium chloride. Table II. (Fig. 13, Curve II.) relates to the penetrating radiation of a specimen of barium-radium sulphate, the intensity of the radiation which traversed 3 c.m. of air and 0·01 m.m. of aluminium having been determined. The two products were subjected to a bright red heat for seven hours.

TABLE I.

Time. Days.	I.
0	16·2
0·6	25·4
1	27·4
2	38
3	46·3
4	54
6	67·5
10	84
24	95
57	100

TABLE II.

Time. Days.	I.
0	0·8
0·7	13
1	18
1·9	26·4
6	46·2
10	55·5
14	64
18	71·8
27	81
36	91
50	95·5
57	99
84	100

I made several other series of determinations, but the results did not agree well.

The effect of heating does not persist when the heated radium compound is dissolved. Of two specimens of the same radium compound of activity 1800, one was strongly heated and its activity thereby reduced to 670. The two portions being now dissolved and left in solution for twenty hours, their initial activities in the solid state were 460 for the not heated portion and 420 for the heated one; the difference between the two portions was therefore not considerable. But if the two products do not remain for a sufficient length of time in solution—if, for example, they are evaporated to dryness immediately after solution—the not heated product is much more active than the heated one; a certain time is necessary in the dissolved state for the effects of heating to disappear. A product of activity 3200 was heated, and its activity thereby reduced to 1030. This product and a similar portion which had not been heated were simultaneously dissolved, and the two then immediately evaporated to dryness. The initial activity was 1450 for the not heated portion, and 760 for the heated one.

In the case of solid radium salts the capacity for exciting induced radio-activity is largely affected by heating. During heating radium compounds give off a larger amount of emanation than at the ordinary temperature; but on being cooled to the ordinary temperature, not only is their radio-activity much less than before heating, but their capacity for inducing activity is much diminished. During the time that follows the heating, the radio-activity of the product increases, and may even exceed the original value. The induction capacity is also partially re-established; however, after prolonged heating to redness, this capacity is almost entirely destroyed without spontaneous reappearance afterwards. The induction capacity may be restored to the radium salt by dissolving it in water, and drying it in the oven at a temperature of 120°. This seems to have the effect of leaving the salt in a peculiar physical condition, in which the emanation is given off with much less facility than is the case with the same solid product not heated to a high temperature, and it follows naturally that the salt attains a higher limit of activity than that which it possessed before heating. To transform the salts into the physical condition proper to it before heating, it suffices to dissolve it and to evaporate it to dryness without heating it above 150°.

The following are numerical examples of the above:—

I represent by a the limit of induced activity produced in a closed vessel upon a plate of copper by a specimen of barium-radium carbonate of activity 1600.

Suppose $a = 100$ for the not heated product. We find—

1 day after heating	$a = 3·3$
4 days ,, ,,	$a = 7·1$
10 ,, ,, ,,	$a = 15$
20 ,, ,, ,,	$a = 15$
37 ,, ,, ,,	$a = 15$

The radio-activity of the product had diminished 90 per cent by heating, but one month afterwards the original value was regained.

The following is an experiment of the same kind made with a barium-radium chloride of activity 3000. The induction capacity is determined in the same manner as before.

For the product not heated $a = 100$.

Induction capacity of the product after being heated to redness for three hours:—

2 days after heating	2·3
5 ,, ,,	7·0
11 ,, ,,	8·2
18 ,, ,,	8·2
Induction capacity of the unheated substance which has been dissolved and then dried at 150°	92
Induction capacity of the heated substance which has been dissolved and then dried at 150°	105

(To be continued).

QUALITATIVE AND QUANTITATIVE ESTIMATION OF TRACES OF ANTIMONY IN THE PRESENCE OF LARGE QUANTITIES OF ARSENIC.

By G. DENIGÈS.

We know how difficult it is to identify and estimate small quantities of antimony by the classic methods, especially when this metal is associated with large quantities of arsenic.

The sensitiveness of the ordinary reactions, with regard to antimony, is very limited, and its separation from the accompanying arsenic becomes impossible to effect when its presence in the products under examination does not exceed fractions of a m.grm. associated with a relatively much higher proportion of arsenic.

Still, the case may occur when we have to detect such small quantities of antimony, either in toxicology or in researches on the elimination of this metalloid.

The methods we are about to describe enable us to detect and estimate quantities of 1/1000th of a m.grm. and less, even in the presence of an amount of arsenic 500 times greater, and, consequently, capable of being used not only in the cases we have mentioned, but also for the detection

of antimony as a possible normal constituent of the organism.

We will deal with these methods in their order of increasing sensitiveness.

1. *Platinum-tin Couple Method.*

When into a hydrochloric acid solution at 25 per cent* of an antimonial product placed in a platinum crucible, we plunge a strip of tin which at the same time touches the platinum, at least by its immersed end, the resulting couple causes, almost instantaneously, the deposition of the antimony on the platinum in the form of a brown stain, when the proportion of this metalloid is not less than 1 m.grm. per c.c. of the hydrochloric solution. With smaller doses the rapidity of the appearance of the stain is a function of the quantity of antimony dissolved in a given volume of liquid, and, for a determined time, the intensity of the brown stain also depends on this quantity; the limit of sensitiveness of the method is 0·04 m.grm. of antimony per c.c. of hydrochloric solution, a dilution which gives an appreciable stain after half-an-hour's contact of the immersed tin and the platinum.

As it is possible to reduce the total volume of the solution containing the antimony to less than $\frac{1}{20}$th of a c.c., we see that 2 1oooths of a m.grm. can be detected in a given sample; for example, in the product of the dissolution of an antimonial ring in nitric acid, evaporated to dryness, and taken up with $\frac{1}{20}$th c.c. of 25 per cent hydrochloric acid. By prolonging the time of contact to an hour the limit may be reduced to 1/1oooth of a m.grm.

When we operate in the same manner with a 25 per cent hydrochloric solution of arsenic acid, no deposit whatever is produced if the quantity of arsenic present does not exceed 5 m.grms. per c.c. of solution; that is 0·5 m.grm. per $\frac{1}{10}$th c.c., and *when the duration of the time of contact does not exceed half-an-hour.*

Beyond that amount, arsenical solutions leave a brownish or even blackish residue when the concentration is great, but the deposit, always relatively feeble, is produced infinitely less quickly than with antimonial solutions of the same strength.

Solutions containing both arsenic and antimony behave in the same manner as antimonial and arsenical solutions alone.

Thus it is possible by this method to estimate with certainity 0·002 m.grm. of antimony in the presence of 125 times as much arsenic.

In practice we use a small platinum crucible with a round bottom, in which is placed the product to be assayed (a ring obtained with Marsh's apparatus, for example), dissolved in a little hot nitric acid, evaporated to dryness on the water-bath ;† take up the residue with a small quantity of 25 per cent hydrochloric acid, sufficient for there not to be more than 5 m.grms. of arsenic per c.c. in the solution, and plunge into the liquid the pointed end of a strip of tin about 1 c.m. wide and 4 or 5 c.m. long, and of such thickness that its weight would be 2 or 3 grms. This strip must be bent at a right angle, so that it rests on the edge of the crucible at one end, and on its point at the bottom of the vessel, in the centre of the solution in which the antimony is being sought for.

It is well to reduce the volume of this solution to $\frac{1}{10}$th or even to $\frac{1}{20}$th of a c.c. After standing the necessary time the crucible is washed with water, alcohol, and ether, and allowed to dry spontaneously; the stain is then distinctly visible.

For the purpose of estimation we proceed by comparison, operating on an equal volume of solutions of antimony in 25 per cent hydrochloric acid, containing per $\frac{1}{10}$th of a c.c. 2, 4, 8, 12, 16, and 20 thousandths of a m.grm. of this metalloid. Each one of these check solutions is placed in a very small platinum crucible or in dents in a strip of the same metal. The strip of tin being immersed by its point as described above,* the checks and the sample are left for the same length of time (half-an-hour for quantities less than 25/1oooths of a m.grm. ; ten to fifteen minutes for quantities greater than this).

We could also base our results, but with less certainty, on the rapidity of the appearance of a stain of a given intensity.

Zinc, which is commonly used for the detection of this body by deposition on platinum, is infinitely less sensitive than tin, and will not answer in the presence of arsenic, even when this metalloid is not in great excess; we have discontinued its use since our very first assay.

2. *Silver-tin Couple Method.*

The silver-tin couple is still more sensitive in the detection of antimony than the preceding couple; it enables us to detect with great ease, after a few minutes contact of the two metals and the solution under examination, 1/1oooth of a m.grm. of antimony contained in $\frac{1}{10}$th of a c.c. of liquid, and in the presence of a thousand times its weight of arsenic, this latter substance having been brought previously to its maximum state of oxidation.

For the actual experiment, we may arrange the drops of liquid to be tested on strips of fine silver, or of commercial silver 900 fine, or even low standard silver 835 fine. The presence of small quantities of copper alloyed with the silver renders the couple even more sensitive. For the purpose of estimation by comparison, as in the simple qualitative search, we make use of triangular strips of tin as described above. In no case should the duration of the contact be more than five minutes.

3. *Cæsium Salts Methods.*

Among the numerous double salts of cæsium examined by Godeffroy in 1876 (*Berichte*, 1876, p. 1365), there are a certain number of well-crystallised ones which, as announced by Behrens, lend themselves to microchemical examination ; among these are the chloride, and especially the iodide of cæsium and antimony. To obtain distinct and constant results, by making use of the formation of this latter salt in the search for traces of antimony, it is necessary to operate under well determined conditions with regard to the concentration of the reagents and the acidity of the medium. After numerous experiments we determined on the following formula, which appeared to us to give the best conditions with regard to sensitiveness with very dilute solutions :—

Dissolve 1 grm. of iodide of potassium and 3 grms. of chloride of cæsium in 10 c.c. of water, and add to the solution 1 drop of 10 per cent commercial ammonia.

When we add the above reagent to a 25 per cent hydrochloric, or a 10 per cent sulphuric solution of antimony, containing at least 2 m.grms. of this metalloid per c.c., there is formed instantly a red precipitate of the double iodide of cæsium and antimony floating in a yellow liquid.

Under certain conditions of formation, this precipitate crystallises in hexagonal plates, yellow or grey, according to their thickness, often grouped in star-like macles ; in the absence of bismuth they are characteristic of antimony.

It is especially with weak dilutions that they are easily obtained; thus they can be observed very well by the careful manipulation of 1 drop of solution containing not more than 1 m.grm. of antimony per c.c. on a strip of glass with 1 drop of the iodo-cæsic reagent.

* Pure commercial hydrochloric acid of density 1·18 (about 36 grms. HCl gas per 100 c.c. of liquid), 1 volume; distilled water 3 volumes.

† It is absolutely necessary, before taking up the residue with dilute hydrochloric acid, for the arsenical product to be brought to its maximum point of oxidation ; for this purpose, after having evaporated to dryness, we take up with a few drops of nitric acid, which must be brought gently to boiling-point, and which must be eventually evaporated to dryness on the water-bath, or else with great precautions in the hot air over a flame.

* In the case of an estimation, and when using dented strips of platinum, we can replace the strip of tin already described by small isosceles triangular sheets of the same metal about 1 or 2 c.m. high, cut from a rectangular strip of the same width, and curved to make a kind of bridge, so that they would stand alone on the sheet of platinum, the apex immersed in the drop under examination, and the base resting on another part of the sheet.

After one or two minutes contact we examine the drop under the microscope, and we perceive very distinct hexagonal crystals, especially in the outer zones of the mixture where diffusion takes place slowly.

Thus it is possible to detect antimony by the production of crystals in an antimonial solution in 10 per cent (by volume) sulphuric acid, containing not more than 0·0001 grm. in $\frac{1}{10}$th of a c.c., a volume to which the sulphuric solutions of the nitric residues of the rings, obtained by means of Marsh's apparatus, can always be brought. In 20 or 25 per cent hydrochloric acid the reaction limit is less distinct and a little less sensitive.

In the presence of arsenic in sulphuric solution we can still detect 1/1000th of a m.grm. of antimony mixed with 500 times the amount of the former body, provided that the strength of the solution (always in 10 per cent sulphuric acid) be not greater than 5 m.grms per $\frac{1}{10}$th c.c. Above this strength there is a tendency to form large rhombic crystals, sometimes hexagonal, of metalloidic iodine, which is set at liberty in acid solution by virtue of the reaction $AsO_4H_3 + 2HI = AsO_3H_3 + H_2O + 2I$, the inverse of that which, in alkaline solution, gives arsenic acid with arsenious acid treated with iodine. Again, with 5 m.grms., and even less, arsenic per $\frac{1}{10}$th c.c. the mixture becomes yellow rapidly, and turns starch blue; to remedy this, when the contact of the stibio-arsenical drop has lasted one or two minutes, we can add a drop of dilute SO_2, which will cause the disappearance, at least momentarily, of the yellow tint, while leaving the specific crystals of antimony undisturbed, and enabling them to show their characteristic red colouration.

Relying on these facts we can recognise the presence of antimony, either in the brown stains obtained with the help of tin, in the method described further back, or in the nitric solution of a mixed stibio-arsenical ring, making use of the evidence of the coloured product of the double iodide of antimony and cæsium, or what is still more certain, the examination of the crystals.

Dealing with the stains on platinum, we add a small drop of nitric acid and evaporate to dryness on the water-bath; with mixed rings we dissolve them in a very small quantity of the same acid, and evaporate the solution collected on as small a surface as possible in a porcelain crucible with a round bottom.

In both cases we place on the dried residue a very small drop (about 1/1000th a c.c.) of the cæsium reagent, which can be spread all over the surface of the residue by means of a finely drawn-out glass rod; then an equal volume (1/1000th of a c.c.) of 10 per cent sulphuric acid is added and mixed with the reagent. After a very short contact we observe a red colour appear, which does not disappear on the addition of a drop of sulphurous acid, and of which the intensity, proportional to the quantity of antimony present, can be used to fix the proportion of this element by comparison with antimonial solutions of known strength.

If we proceed in the inverse manner and first moisten the residue with 25 per cent hydrochloric acid, and then place a small drop of the cæsium residue very carefully in the centre of the moistened portion, we observe, after the lapse of two or three minutes, the appearance of the characteristic hexagonal crystals in one drop of the mixture placed on a glass slip for microscopic examination,

Finally, if the amount of antimony in the residue is at least $\frac{1}{100}$th of a m.grm., this residue can be dissolved in $\frac{1}{10}$th of a c.c. of 25 per cent hydrochloric acid; place a drop of the solution on a glass slip, then in the centre of this drop place an equal volume of the iodo-cæsic reagent very carefully, wait about two minutes, and examine under the microscope, either with or without the addition of sulphurous acid, according to whether there is more or less arsenic in the mixture.

It will be easily understood that the same methods apply *a fortiori* to the rapid detection of antimony and arsenic in saline solutions; the substance examined being placed in a test-tube containing pure zinc, a drop of sulphate of copper, and 10 per cent (by volume) sulphuric acid, fitted with a curved drawn-out tube for lighting the resultant gas; this will give stains on porcelain which can be used for the definite analysis.

The stain on the porcelain, dissolved in a very small quantity of nitric acid, is, after careful evaporation, taken up again with nitric acid, then again evaporated to dryness, and if necessary treated finally with a little bromine water, and once more evaporated to effect the complete oxidation of the arsenic; this will give a residue which, when taken up with a few drops of 25 per cent hydrochloric acid, will give a liquid of which a portion placed on a sheet of platinum or silver, or even a silver coin, will rapidly show a brown stain if it contains antimony, and of which another portion will give a red precipitate with the characteristic crystals, insoluble in a small quantity of sulphurous acid.

The stain from another crucible lid, dissolved in two drops of nitric acid, then treated with from a quarter to half a c.c. of sulpho-nitro-molybdic reagent, will give a solution which, when heated on the water-bath, will give a yellow precipitate if it contains arsenic.—*Bulletin de la Société de Pharmacie de Bordeaux*, January, 1903.

ACTION OF ULTRA-VIOLET LIGHT UPON RARE EARTH OXIDES.

By CHARLES BASKERVILLE.

During the extended investigations of the action of ultra-violet light, Röntgen rays, cathode rays, and the emanations of radium upon gems and mineral in the Morgan-Tiffany gem and Morgan-Bement minerals collections in the American Museum of Natural History, a number of rare earth oxides were subjected to the action of ultra-violet light. The following oxides were exposed to ultra-violet light produced by a Piffard lamp:—

Gadolinium oxide (prepared by Waldron Shapleigh).
Lanthanum oxide (prepared by H. S. Miner).
Neodidymium oxide (prepared by a method of Baskerville and Stevenson).
Praseodidymium oxide (prepared by the method of Baskerville and Turrentine).
Cerium oxide (prepared by H. S. Miner).
Samarium oxide (prepared by Waldron Shapleigh).
Thorium dioxide (chemically pure, according to general acceptation previous to 1900; prepared by Baskerville and Davis).
Yttrium oxide (prepared by Waldron Shapleigh).
Yttrium, erbium, and ytterbium oxides mixed (prepared by H. S. Miner).
Erbium oxide (bought from Kahlbaum).
Erbium group oxides (prepared by Benton Dales).
Uranium oxide, Uranium oxide (prepared by S. Auchmuty Tucker).
Yttrium oxide (prepared by Dennis and Dales).
Titanium oxide (purchased from Eimer and Amend).
Ytterbium oxide (prepared by Benton Dales).
Zirconium dioxide (prepared by Venable and Baskerville).

(My thanks are due to Drs. Miner, Tucker, and Dales for the generous loan of preparations).

Only two of the above oxides responded at all to the action of ultra-violet light—namely, zirconium and thorium dioxides, which phosphoresced strongly. The thorium dioxide remained luminous in the dark for a greater length of time. The zirconium dioxide showed no radio-activity when tested by the electrical and photographic methods. It is strange that the two rare earths forming normally the dioxide are the only ones to exhibit this property. This will be investigated further.

In view of the fact that these two earths give this characteristic response to ultra violet light, it became immediately of interest to learn the effect of the light upon minerals carrying those substances in different proportions.

The following minerals were subjected to the action of ultra-violet light without a single one of them giving either fluorescence or phosphorescence:—

Samarskite—Bertheir County, Quebec.
Thorite (Orangite)—Arendal, Norway.
,, —Barkevik, Norway.
,, (Auerlite)—Green River, North Carolina.
Sipylite—Amherst County, Virginia.
Columbite—Portland, Connecticut.
Monazite—Arendal, Norway.
,, Zlatoust, Ural.
,, 171st Street and Washington Avenue, New York.
,, Amelia C. H., Virginia.
,, Alexander County, North Carolina.
Monazite Sand—Rio, Brazil.
Monazite—Tyedestrand, Norway.
Xenotime—Cheyenne Cañon, Colorado.
,, Alexander County, North Carolina.
,, Hitteroe, Norway.
Euxenite (in Samarskite) — Mitchell County, North Carolina.
Æschynite—Hitteroe, Norway.
Polycrase—Near Marietta, South Carolina.
Fergusonite—Llano County, Texas.
,, Ytterby, Sweden.

The extended investigation of the action of ultra-violet light upon minerals carried out by Dr. Geo. F. Kunz and the writer will shortly be published in full.

University of North Carolina,
September 15, 1903.

ON THE THEORY OF DYEING.

By EDMUND KNECHT.

In an article which appeared in No. 11 of the *Zeitschrift fur Farben- und Textil-Chemie*, 1903, von Georgievics points out that he has been unable to confirm Knecht's observations (*Ber.*, 1902, p. 1022), that wool and silk, dyed with night-blue, yield to boiling alcohol compounds, both of which, when decomposed with barium hydrate, leave in solution an organic substance which is again capable of producing coloured lakes with either night-blue or magenta. He suggests that Knecht's results were due to impurities in the materials employed, and furthermore maintains that night-blue alone, without the intervention of any fibre, when treated with barium hydrate and filtered from the precipitated base, yields, after the removal of excess of barium hydrate, a substance which is capable of precipitating magenta. From the results thus obtained, von Georgievics considers himself justified in condemning Knecht's conclusions.

The author now gives an account of a repetition of his original experiments. The wool employed was a good quality of flannel, which was first extracted for eight hours in a Soxhlet with alcohol, and then twice with boiling distilled water. The wool thus purified was dyed at the boil for one hour with 2 per cent night-blue in a bath acidulated with acetic acid. It was then extracted with alcohol in a Soxhlet until the upper portions of the material were decolourised. The alcoholic solution was evaporated down to a small bulk and added to a warm dilute solution of barium hydrate, which resulted in instant decolorisation and separation of the night-blue base. The filtered solution was treated at the boil with carbonic acid, filtered from the separated barium carbonate, and evaporated to dryness. An amorphous yellowish coloured residue was obtained which, when heated on platinum foil, emitted the well-known smell of burning wool. Dissolved in water, this residue was found to yield with both night-blue and with magenta the precipitates mentioned in the original paper. Both were soluble in alcohol. It was further found that this mild treatment with barium hydrate did not effect a complete decomposition of the colour lake, since the residual night-blue base, when treated with hot ammonia, yielded to the solution further quantities of a yellowish substance which showed similar properties to the first.

The experiments on silk were done with a sample of boiled-off Japan silk, which was purified first by extraction with alcohol and then with distilled water. The further treatment was the same as in the case of wool. In this case also, a yellowish coloured residue resulted, the aqueous solution of which precipitated both night-blue and magenta. As was found to be the case with wool, the precipitated night-blue base retains some of the lake-producing substance.

Referring to the observation made by von Geogievics that night-blue itself, when treated with barium hydrate, yields, after gassing with carbonic acid, a solution capable of precipitating magenta, the author draws attention to the fact that this solution contains, besides cane-sugar, both barium chloride and sodium chloride. The precipitates which it gives with night-blue and with magenta are simply mechanical in character and are readily dissolved on washing with water, whereas those obtained from the alcoholic extracts of the dyed fibres are not dissolved. As the result of his renewed investigations, the author, while entirely refuting von Geogievics' evidence, claims to have fully confirmed his original conclusions regarding the nature of the dyeing process.—*Zeitschrift fur Farben- und Textil-Chemie*, No. 16, 1903.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month ending October 31st, 1903.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Charles Perrin, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, November 10th, 1903.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 220 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from October 1st to October 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 220 samples examined by us during the month, 219 were clear, bright, and well filtered, and one sample was clear but dull.

The rainfall at Oxford during October has been greater than in any previous month this year, and rain fell on twenty-five days out of the thirty-one; the amount registered was 6·41 inches. The average rainfall for the month being 2·76 inches, we have an excess of 3·65 inches. This, added to the previous one of 8·92 inches, makes a total excess for the year of 12·57 inches, or 60·3 per cent above the thirty-five years' average.

Our bacteriological examinations of 376 samples taken during the last month have given the results recorded in

the following table. Besides these samples we have examined 399 others from special wells, standpipes, &c., making a total of 775 samples in all :—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	843
New River, filtered (mean of 56 samples) ..	30
Thames, unfiltered (mean of 27 samples)	16,671
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 214 samples)	66
Ditto ditto .. .. highest	558
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 27 samples) ..	470
River Lea, from the East London Water Company's clear-water wells (mean of 27 samples)	25

Of the 297 daily samples taken from the filter wells of the Metropolitan Water Companies, twelve samples, or 4 per cent, were sterile. Fifty-one samples, or 17·1 per cent, contained more than 100 microbes, and of these, thirty-four samples contained more than 150 microbes per c.c. The fifty-one excess samples contained an average of 186 microbes per c.c. In September twenty-seven excess samples contained an average of 182 microbes per c.c. It will be noticed therefore that, although an excess in the number of microbes has been more frequent during the month, the average character of the samples has not deteriorated.

It must be observed that the number of samples collected containing more than 100 microbes has increased during the course of October to double the number of the September samples. The general microbic character, however, of the excess samples of either month was found to be substantially the same. Considering the generally flooded condition of the valleys of the Thames and Lea during nearly the whole of October, the filtration of the general supply has been well conducted, and would have been better if the number of filters undergoing cleaning had been diminished in the case of some of the Companies. The exceptional rainfall, now amounting to 60 per cent in excess of the average, keeps both the colour and the amount of soluble vegetable matter in solution abnormally high. While the average organic carbon in the supply from the Thames has increased, that of the East London supply from the Lea has diminished during the course of last month. The large storage reservoirs on the Lea no doubt account for this difference.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

Estimation of the Lower Oxides of Molybdenum and of Metallic Molybdenum.—C. Friedheim and M. K. Hoffmann.—The authors deal first with the preparation of binoxide of molybdenum. MoO_3 is calcined for from five to seven hours at 450° in a current of hydrogen, then at a dull red heat in a current of dry hydrochloric acid. After several repetitions of these treatments, pure MoO_2 remains, perfectly free from MoO_3. Dealing next with the methods for the estimation of the oxides lower than MoO_3, or of metallic molybdenum, they proceed by heating these products to boiling with a titrated solution of ammonio-ferric sulphate acidulated with sulphuric acid, and estimate the ferrous sulphate formed by means of permanganate of potassium. An indirect estimation could also be made by treating the lower oxides of molybdenum, or the metal, by a very dilute ammoniacal solution of nitrate of silver. The reduced silver is collected on a filter, and the silver remaining in solution is estimated. This plan has been recommended already by other chemists.—*Berichte*, vol. xxxv., p. 791.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, November 5th, 1903.

Prof. Tilden, D.Sc., F.R.S., President, in the Chair.

Messrs. C. N. Bennett, G. Barger, H. Gough, W. Mann, C. D. Bibby, and S. H. Woodhouse, were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Robert Duncombe Abell, Ph.D., D.Sc., Sandbach, Cheshire; Percy Appleyard, Albany, Western Australia; Edward F. Armstrong, Ph.D., 55, Granville Park, Lewisham, S.E.; Herbert Henry Ashdown, 3, Genesta Road, Plumstead; Herbert Moore Attwell, Limpley Stoke, Bath; William C. Badcock, B.A., The Grammar School, Crediton, Devon; Harold J. Bailey, 40, The Avenue, Pontypridd, South Wales; Thomas Vipond Barker, Exeter College, Oxford; Charles Marsh Beadnell, H.M.S. Barracouta, Capetown; William Beam, M.A., M.D., Pension Sima, Cairo, Egypt; Harold Goodenough Bayly, "Moatside," Bedford; Henry James Wheeler Bliss, Balliol College, Oxford; Nicholas John Bluman, 10, Amersham Road, New Cross, S.E.; Paul Brühl, Engineering College, Sibpur, near Calcutta; Erasmus Robert Buggé, 327, Grove Green Road, Leytonstone; William Clacher, Bryantwood, Auckland Road, Ilford; William Thomas Deeks, High Street, Shanklin, I.W.; Henry Russell Ellis, 177, Warwick Road, W.; Charles E. Fawsitt, Ph.D., B.Sc., 9, Foremount Terrace, Glasgow; John A. N. Friend, M.Sc., 2, Francis Road, Watford, Herts; Ernest A. Gardiner, B.A., Bretherton, near Preston, Lancs.; Frank B. Gatehouse, 56, Windmill Street, Gravesend, Kent; Frank B. Grundy, Red Lodge, King's Road, Richmond, S.W.; John T. Hall, West View, Stanwell, Staines; Harold M. Heasman, 1, Carlisle Road, Finsbury Park, N.; Arthur V. Hendrickson, Gas Works, Lower Sydenham, S.E.; John G. Howarth, "Danes Dyke," Capstone Road, Bournemouth; Herbert Hymans, 13, Trinity Square, E.C.; Edward Charles Ibbotson, 3, Ashgate Road, Sheffield; William H. Jackson, 73, Church Street, West Hartlepool; Thomas Oliver Kent, 89, Loughboro' Park, Brixton, S.W.; John J. Kielty, 71, Cairo Road, Walthamstow; Harley F. Knight, 64, Amhurst Park, Stamford Hill, N.; John Laing, Everlie, Skelmorlie, N.B.; Francis E. E. Lamplough, B.A., Trinity College, Cambridge; Harold Duff Leadbetter, 95, Capel Road, Forest Gate, E.; Gervaise Le Bas, B.Sc., Baymount House, St. Aubins, Jersey; David B. Macdonald, 18, Kimberley Road, Leicester; Frederick W. McMahon, 61, Brockley Rise, Forest Hill, S.E.; Ernest W. Mann, Willow Avenue, Edgbaston, Birmingham; Gordon W. Monier-Williams, B.A., The Lammas, Esher, Surrey; Urban O. S. Nairne, 7, Hawthorne Terrace, Barking, Essex; James Victor Nevin, Bristol Dispensary, Bristol; Henry George Pike, Downton, Salisbury, Wilts; George Horace G. Plymen, 2, Melton Road, Leicester; William Branch Pollard, B.A., 68, Finnart Street, Greenock, N.B.; Stiles W. G. Rich, Stanley Street, South Brisbane, Queensland; Harold E. Richardson, B.A., B.Sc., 63, Lansdowne Road, Ilford; William David Rogers, 36, Grange Road, Smethwick; George Senter, Ph.D., B.Sc., 37, Ronalds Road, Highbury, N.; Arthur Slator, Ph.D., M.Sc., The Priory, Burton-on-Trent; William V. Smith, B.A., 7, Grove Road, Ipswich Road, Norwich; A. W. Stewart, B.Sc., 18, Annfield Terrace, Partick Hill, Glasgow; Arthur Tighe, 20, Marlborough Place, St. John's Wood, N.W.; Arnold Turner, 316, Entwistle Road, Rochdale; William E. S. Turner, B.Sc., 52, Cheshire Road, Smethwick; Miles Walker-Pole, Braamfontein, Johannesburg; Carl F. R. Weiss, Ph.D., M.A., Victoria Park, Manchester; Fred Wright, Terry Street, Balmain, N.S.W.

Certificates in favour of the following were authorised by the Council for presentation for ballot under By-law I. (3): —Thein Kin, Rangoon, Burma; Mata Prasad, Benares, India; P. W. Robertson, Wellington, New Zealand.

The PRESIDENT announced that the Council had decided that a supplementary number of the *Transactions* should be issued on December 31, and that after that date the *Journal* would be issued on the last day of each month instead of the first day of the month as hitherto, the first number for 1904 being issued on January 31st.

The PRESIDENT then reminded the Society of the announcement he had been permitted to make at the meeting on May 20th in reference to the bust of Dalton which was now before them, and read the following letter from Prof. Thorpe.

Government Laboratory, London, W.C.,
October, 1903.

DEAR MR. PRESIDENT,—Although the walls of the Society's apartments are adorned with busts, medallions, and other mementoes of eminent chemists, there is among them no memorial of one of the most illustrious of all chemists—John Dalton.

As a fellow-townsman of Dalton, may I be permitted, in grateful remembrance of the fact that my early education was promoted by a studentship founded in his memory and associated with his name, to supply, in some small measure, the lack of such a memorial, and to ask that the Council will do me the honour to accept the bronze bust which accompanies this letter?

As you are aware, this month one hundred years ago saw the promulgation of Dalton's great generalisation. There is, therefore, I venture to hope, a special fitness in preferring my request at this particular time.

The bronze is the work of Miss Levick, who is already known to the Society by her reproduction of the bust of Davy in their possession. Of the artistic merits of her present work others must be the judge, but I may be permitted here to express my indebtedness to her for the skill and conscientious care with which she has striven to make a faithful and adequate presentment of the grand old philosopher. She has been greatly assisted by the kindness and co-operation of many friends to whom my acknowledgments are due. Practically all the available material has been placed at her disposal—the copy of the well-known Chantrey bust in the possession of the Literary and Philosophical Society of Manchester; the Cardwell bust belonging to Owens College; a beautiful but little known steel engraving by Stephenson, given to me by my friend Dr. Blackley; the portrait in the possession of the Royal Society; the precious daguerreotype formerly in the possession of Dalton's friend and pupil the late Mr. John Dale, and now the property of the Society; together with a number of other drawings and engravings.

I am gratified to know that those who are competent to form an opinion have expressed the conviction that Miss Levick has made admirable use of her ample material, and that she has succeeded not only in reproducing the lineaments of the great chemist, but in infusing into them a conception of the simplicity, dignity, and grandeur of his character.—I am, Dear Mr. President, faithfully yours,

T. E. THORPE.

The Council had that afternoon passed a resolution tendering to Dr. Thorpe an expression of most cordial thanks for his generous and interesting gift.

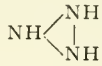
Of the following papers, those marked * were read:—

*130. "*The Reduction of Hydrazoic Acid.*" By W. T. COOKE,

Apart from Peratoner and Oddo's observation (*Gazzetta*, 1895, xxv., 2), that ammonia is formed at the cathode when hydrazoic acid is electrolysed, the behaviour of hydrazoic acid when subjected to reducing agents does not appear to have been studied.

Considering the acid as a cyclic compound having the formula—

the first step in its reduction should lead to the formation of the hydride,—



but the existence of this hypothetical compound seems doubtful in view of the ease with which nitrogen hydrides pass into ammonia. On the other hand, boron, which has even less affinity for hydrogen than nitrogen, forms the corresponding hydride, B_3H_3 (Ramsay and Hatfield, *Proc.*, 1901, xvii., 152), so that N_3H_3 may possibly exist as a gas with feebly basic properties. Further reduction would, however, result in the breaking up of the ring, with the formation of ammonia, and possibly hydrazine, as an intermediate product. These substances were actually obtained when the following reducing agents were tried:—Sodium amalgam, zinc, and either hydrochloric or sulphuric acid, sodium polysulphide, and ferrous hydroxide.

Ammonia was the chief product, and the hydrazine, which was generally present in small quantities, was obtained in appreciable amount only in those experiments where it was removed from solution in the form of an insoluble compound during the reaction. It may, however, be formed at first in accordance with the equation $NH{\cdot}N_2+3H_2=NH_3+N_2H_4$, and then at once reduced, for trial reduction experiments, in which hydrazine sulphate was used instead of hydrazoic acid, showed that some ammonia was formed.

The hydrazoic acid was made by the method devised by Wislicenus (*Ber.*, 1892, xxv., 2084), and was employed in approximately decinormal solution.

The products of reduction were separated from the mixture by distillation from an alkaline solution, the distilling flask being provided with a "Kjeldahl" bulb; in most cases, the distillates, when acidified with hydrochloric acid and concentrated, showed a slight reducing action towards ammoniacal silver nitrate, Fehling's solution, &c.; the residues in the distilling flasks also produced the same effect. This result might be anticipated since hydrazine hydrate is less volatile in steam than ammonia. The latter substance was recognised by its odour, alkalinity, reaction with Nessler's reagent, and the analyses of its platinichloride.

In reducing with sodium amalgam, the solid reagent was slowly added to separate quantities each consisting of 50 to 100 c.c. of acid, so as to maintain a slight effervescence. After about a week, the liquid was decanted from the mercury and distilled. Reduction proceeded more quickly in acid solution, but the hydrazoic acid was easily lost.

The addition of sodium amalgam to freshly precipitated silver hydrazoate, which had been carefully washed until free from acid, and suspended in water, caused the separation of silver, which partly went into solution in the colloidal condition, giving the liquid a dark brown colour.

The hydrazoic acid readily attacked zinc, and when the effervescence had subsided, sulphuric, or occasionally hydrochloric, acid was gradually added in small quantities. In the case of sulphuric acid, a granular deposit of the double salt, $(N_2H_4)_2H_2SO_4,ZnSO_4$ (*Ber.*, 1893, xxvi., 410), was formed on allowing the reaction to continue for at least a week.

A solution of this salt, which is fairly soluble in hot water, easily reduces an acid solution of gold chloride. The precipitate of cadmium sulphide obtained on mixing solutions of cadmium hydrazoate and sodium polysulphide was collected after a few days, when the filtrate was found to contain a small quantity of ammonia.

An alkaline solution of sodium hydrazoate was used in the case of ferrous hydroxide, and the reduction was carried

on at the boiling temperature in a current of hydrogen, the ammonia evolved being collected in dilute acid. The mixture in the flask was distilled while still alkaline, and again when acidified with sulphuric acid, the latter operation being performed in order to recover the unused hydrazoic acid.

Similar experiments were also made on the reduction of hydrazine sulphate with zinc or sodium amalgam; in both instances a small amount of ammonia was formed. In the case of zinc and sulphuric acid, the formation of an appreciable amount of hydrogen sulphide was noticed at the beginning of the reduction.

These results show that it is possible by the use of reducing agents to split the hydrazoic ring, and that there is certainly no tendency for the ring to become saturated by the addition of two atoms of hydrogen.

*131. "*Preliminary Note on the Viscosity of Liquid Mixtures.*" By A. E. Dunstan and W. H. C. Jemmett.

Three typical liquid mixtures have been used in this research, namely: (1) ethyl acetate and benzene; (2) benzene and ethyl alcohol; (3) ethyl alcohol and water.

The apparatus used was of Ostwald's pattern; the viscometer was immersed in a bath, which was kept at 25° by means of a thermostat, and was stirred by a current of carbon dioxide.

In the first mixture, which consisted of a pair of non-associative unimolecular liquids, the viscosity was an additive property, and an almost straight line curve was obtained having a slight concavity. Neither liquid has much effect on the other; the concavity probably indicates slight association.

A similar result was also obtained in the case of a mixture of benzene and carbon disulphide.

In the second mixture, where only the alcohol was associative, a minimum point was reached when about 6 per cent of alcohol was present; the remaining part of the curve was normal. This minimum point is probably due to further association of alcohol molecules. It has been shown in freezing point determinations that alcohol in benzene gives abnormally high results, and Pickering has recognised a break in the freezing point curve corresponding with 6 per cent of alcohol.

In the third case both liquids are associative, and as the percentage of either constituent increased there was a strongly marked rise of viscosity, which culminated in a maximum point, corresponding with 55·83 per cent of alcohol. At this point the proportion of alcohol and water is very approximately 2 mols. water to 1 mol. alcohol. I. Traube (*Ber.*, 1886, xix., 871) indicates maxima of a similar nature for this mixture at about 46—50 per cent alcohol. Pickering has shown that in the freezing point curve of alcohol in water there is a break at 53 per cent (*Trans.*, 1893, lxiii., 1012).

In the case of the third mixture each substance possibly dissociates the associated molecules of the other, thus giving rise to an increased number of active particles. Jones and Murray (*Amer. Chem. Journ.*, 1903, xxx., 193) have shown that such dissociation is the case for several associative bodies. This would explain the gradually increasing viscosity up to the maximum point corresponding with $2H_2O—C_2H_5OH$.

The work is being extended to other liquid mixtures.

*132. "*A Contribution to the Study of the Reactions of Hydrogen Peroxide.*" By J. McLachlan.

When solutions of hydrogen peroxide and potassium bichromate are mixed and boiled with sulphuric acid, the volume of oxygen evolved is not equal to twice the available oxygen of the hydrogen peroxide. The available oxygen in the peroxide solution was estimated by iodometry, the object being to find the available oxygen in 0·56 c.c. of the sample of the peroxide, as this figure represents the volume of 0·0008 grm. of oxygen. It is essential that the solution of the peroxide should be dilute, and the sulphuric acid solution should not be stronger than 1 in 5. When stronger solutions of sulphuric acid are added to a solution of potassium iodide, a considerable quantity of iodine is set free before the peroxide solution is added.

The proximate cause of the ready production of iodine when stronger solutions of sulphuric acid are added to a solution of pure potassium iodide is believed to be dissolved oxygen. If, in such a solution containing some starch paste, the blue colour is destroyed by a drop or two of a centinormal sodium thiosulphate solution, the colouration reappears after a definite number of minutes. This regeneration of the blue colour, after its destruction by the thiosulphate solution, will go on for weeks, perhaps for months or even years, until either the potassium iodide or the sulphuric acid has been used up. With hydrochloric acid the blue colour is reproduced in about one-seventh of the time required for its reappearance when the equivalent amount of sulphuric acid is employed, and hydriodic acid is almost as active. Tartaric acid is about as active as sulphuric acid, phosphoric acid not quite so active, oxalic acid still less so, whilst with boric acid the time required for the development of the blue colour is about four days.

The estimation of the available oxygen in a solution of peroxide of hydrogen by an acidified solution of potassium permanganate has been found to be utterly untrustworthy.

Estimations have been made of the available oxygen of manganese dioxide (1) in its original state, (2) after being boiled with a solution of hydrogen peroxide, (3) after being boiled with a solution of hydrogen peroxide and sulphuric acid, the process employed being the oxalic method, in which a known weight of manganese dioxide, mixed with a known volume of a normal solution of oxalic acid, and excess of sulphuric acid (1 in 3) is heated until the whole of the dioxide is decomposed, and the excess of oxalic then estimated by a standard solution of potassium permanganate. The hydrogen peroxide solution should be added only after the manganese dioxide and sulphuric acid are thoroughly mixed.

The results indicate that (1) the manganese dioxide is not decomposed by the hydrogen peroxide in accordance with the equation $MnO_2+H_2O_2=MnO+H_2O+O_2$, as in reality only a portion of the oxygen is evolved; (2) the presence of sulphuric acid is absolutely essential, for without it the foregoing reaction does not occur.

Discussion.

Dr. Divers said that his own experience, as well as that of others, was that a mixture of *pure* potassium iodide and *pure* sulphuric acid if sufficiently dilute would remain colourless in the dark for hours in the presence of starch, even when exposed in an open vessel. In contact with the air, such a likely impurity as a very minute quantity of nitrous acid, although too small to cause an immediate effect, acted slowly as a carrier of oxygen and produced an intense colouration.

Dr. McLachlan, in reply, said that every effort was made to secure pure potassium iodide. Moreover, the action of traces of iodate or nitrous acid would not be an adequate explanation of the phenomena, unless such substances were normal constituents of the atmosphere as distinct from the air of a chemical laboratory.

*133. "*The Constitution of certain Silicates.*" By C. Simmonds.

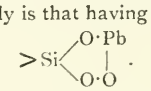
Silicates of lead, copper, iron, cobalt, and nickel are reduced when heated to redness in hydrogen, and as a rule a silicate containing x atoms of lead or copper yields x atoms of oxygen. A few naturally occurring ferruginous silicates behave exceptionally under these conditions, some giving up only a portion of the corresponding oxygen, whilst others yield none. The reduced silicates are black powders which, except in the case of lead orthosilicate, do not appear to contain any notable amount of the reduced element in the metallic state.

The formulæ usually adopted do not furnish a simple interpretation of the results obtained on reduction. In lead metasilicate, $O:Si<^{O}_{O}>Pb$, for example, the two oxygen atoms connected with the metal are represented as

occupying precisely similar positions in the molecule, and there is no apparent reason why only one should be removed by hydrogen.

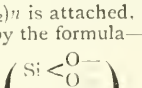
The formula of such a silicate ought, however, to indicate that at least one atom of oxygen (the displaceable one) is attached to each atom of lead, and also that this labile oxygen is linked to the metal in a manner differing from the mode of attachment of any other oxygen atom.

The configuration which satisfies the prescribed conditions most completely is that having the grouping—

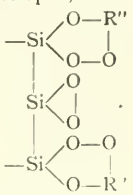


The following conclusions have been deduced :—

(*a*) The silicon atoms are in direct combination with one another, and not joined by means of oxygen. (*b*) To the chain of silicon atoms thus formed the oxygen corresponding with $(SiO_2)n$ is attached, giving rise to a mode of grouping denoted by the formula—



(*c*) The oxygen valencies still unappropriated are those by which the basic oxides (PbO, CuO, &c.) become attached to the silica complex. (*d*) The conception of silicate structure to which these deductions lead is that of a chain, either closed or open, of the following type :—



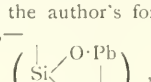
The two free silicon valencies would presumably unite, the silicate thus acquiring a closed chain or ring structure. Or they may possibly be connected by another molecular group—Al_2O_3, for instance—also giving rise to a ring. They might also conceivably be attached to any univalent atoms or groups, thus forming an open chain.

Whether the above type of structure is the rule or the exception is at present uncertain, but that some diversity exists is shown by the behaviour of those ferruginous silicates (for example, staurolite, augite, and epidote) which are not reduced by hydrogen at a red heat. Possibly, although not necessarily, these differences may be due to the occurrence of an entirely different kind of structure.

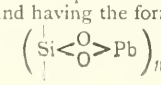
The natural silicates which have, so far, been found to undergo practically complete reduction (in the sense already explained) are dioptase, chrysocolla, garnierite, connarite, chloropal, glauconite, cronstedtite, and thuringite. Ilvaite and stilpnomelane show considerable, but not complete, reduction, this action being much less marked in the case of hypersthene.

Discussion.

Mr. C. E. Groves asked the author whether he had treated the *reduced* lead silicate with pure mercury and some acid, such as acetic acid, which did not act either on lead or mercury in order to ascertain whether the lead present in this reduced residue was in the metallic state. If it were not, and the author's formula for lead metasilicate, for instance,—



be accepted, the reduced product must be a remarkable lead-silicon compound having the formula—



Mr. Simmonds, in reply, said that he had experimented with mercury, but not with acetic acid, when testing the reduced silicate residues for metallic lead, and he hoped to deal with the matter more fully at some future date. The composition of these residues, however, was a question quite distinct from the one discussed in the paper.

*134. "*The Constitution of Chrysophanic Acid and of Emodin.*" By H. A. D. Jowett and C. E. Potter.

The authors discussed the evidence bearing on the positions of the substituting groups in the formulæ for chrysophanic acid and emodin. They concluded that chrysophanic acid must be represented as 5 : 8 dihydroxy-1-methylanthraquinone, as previously suggested by Hesse, and emodin as 2 : 5 : 8- or 3 : 5 : 8-trihydroxy-1-methylanthraquinone.

Emodin, on fusion with caustic alkali or on oxidation with permanganate, yielded no definite product.

By the action of sodium and methyl iodide on emodin, only the *monomethyl ether*, $C_{16}H_{12}O_4$ (m. p. 200°), was formed; its *diacetyl* compound melts at 157°. This emodin methyl ether appeared to differ from the naturally occurring product obtained by Perkin (*Trans.*, 1894, lxv., 932). Attempts to synthesise the foregoing di- and trihydroxymethylanthraquinones by the condensation of hydroxysalicylic acid with substituted *o*- and *m*-toluic acids, and also of 1-methylphthalic anhydride with quinol, were unsuccessful.

By the condensation of two molecules of hydroxy-*p*-toluic acid ($CH_3 : OH = 1 : 2$), three isomeric dihydroxydimethylanthraquinones were produced.

3 : 5-*Dihydroxy*-2 : 6-*dimethylanthraquinone*, $C_{16}H_{12}O_4$, which formed yellow leaflets not melting below 300°, yielded a *diacetyl* compound (m. p. 215°) and a *monomethyl ether* (m. p. 214—215°); the latter formed a *monoacetyl* compound (m. p. 195—196°).

1 : 5-*Dihydroxy*-2 : 6-*dimethylanthraquinone* formed red needles (m. p. 224—225°), did not yield a methyl ether, and was insoluble in dilute ammonia.

3 : 7 - *Dihydroxy*-2 : 6 - *dimethylanthraquinone* formed orange-yellow needles (m. p. 232°) and readily dissolved in dilute ammonia to a red solution.

135. "*Conductivity of Substances Dissolved in certain Liquefied Gases.*" Preliminary Notice. By B. D. Steele and D. McIntosh.

The authors have studied the behaviour of salt solutions in hydrogen chloride, bromide, iodide, sulphide, and phosphide.

In view of the known dissociation of salts when dissolved in hydrogen fluoride, water, or liquefied ammonia gas, it was anticipated that the foregoing solvents would all behave as ionising media. This anticipation has, however, been only partially realised.

In hydrogen chloride solution, sodium chloride, potassium iodide, ferric chloride, and water do not conduct at all; potassium permanganate, sodium acetate, ammonium oxalate, and ammonium chloride diminish the resistance only very slightly, whilst potassium cyanide and several haloid salts of the amines yield highly conducting solutions.

Trichloroacetic acid, sodium chloride, and water do not conduct in hydrogen bromide solution; potassium iodide and potassium bromide conduct very slightly, whereas ammonium acetate, potassium cyanide, diethylammonium chloride, and tetramethylammonium chloride conduct well.

Potassium cyanide, potassium iodide, phosphonium iodide, and water do not diminish the resistance of hydrogen iodide solution, whilst the haloid salts of the amines reduce it considerably.

In hydrogen sulphide solution, hydrochloric acid, sulphuric acid, sodium chloride, and sodium sulphide do not conduct, ammonium chloride conducts only slightly, but ammonium sulphide and the salts of the amines greatly diminish the resistance of the solvent.

Phosphonium iodide, potassium iodide, sodium acetate, ammonium acetate, potassium cyanide, and the salts of the

amines do not appreciably reduce the resistance of hydrogen phosphide.

The salts of some of the ammonium bases greatly reduce the resistance of the first four solvents but do not diminish that of liquefied phosphine, and no salt has yet been found which will reduce to any appreciable extent the resistance of this solvent.

It is at present impossible to state whether the cases of non-conduction are due to the insolubility of the salts or to solution unaccompanied by ionisation, but systematic quantitative experiments are being made on the foregoing solvents.

136. "*The Behaviour of Metallic Oxides towards Fused Boric Anhydride.*" By C. H. BURGESS and A. HOLT, jun.

The authors have investigated the action of fused boric anhydride on many metallic oxides, and find that only a limited number dissolve. Lithium, sodium, potassium, cæsium, and rubidium, as carbonates, readily dissolve in boric anhydride in all proportions up to saturation, giving clear glasses, and thallium behaves in the same way. With a very large amount of alkali, however, the glass becomes opaque.

Calcium, strontium, barium, zinc, cadmium, magnesium, manganese, lead, and bismuth oxides are insoluble in small quantities, but on gradually increasing the amount, dissolve to clear glasses; with a further addition of oxide, the mass again becomes opaque except in the cases of lead and bismuth, which yield pale yellow, very fusible glasses.

The oxide of mercury appears to be soluble, and those of antimony and arsenic slightly so. The oxides of aluminium, beryllium, zirconium, tin, cerium, thorium, niobium, and silicon are all quite insoluble. The oxides which colour the borax bead, namely, those of chromium, copper, molybdenum, uranium, iron, nickel, and cobalt, are all insoluble in the fused anhydride, the manganese oxides in this respect behaving exceptionally.

The last series of oxides can, however, be dissolved in boric anhydride containing lithium, potassium, cæsium, rubidium, and thallium, and the clear glasses obtained with large amounts of the coloured oxides were similar to the borax beads although the colours were sometimes modified.

(To be continued).

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Presidential Address.

AT a meeting of the above Society, held in the Chemistry Tutorial Class Room, University New Buildings, Edinburgh, on Monday, November 9th, 1903, Prof. CRUM BROWN delivered his Presidential Address on "*Electricity as a Chemical Element.*"

Starting from the assumptions (1) of the doctrines of Electrolytic Dissociation, and (2) that "resinous" or "negative" electricity is the only real electricity ("vitreous" or "positive" electricity being merely the lack of this), and that this real, resinous electricity is material, and consists of atoms (Lord Kelvin's "Alpinus atomised"), Prof. Crum Brown developed certain consequences as to the constitution of the ions of electrolysis and of some substances, specially of amino-acids and betaines.

Platinised Aluminium Dishes.—A. Gawalowski.—Polished aluminium is easily platinised by contact with a 5 or 10 per cent solution of chloride of platinum, to which is added enough potash to give it a slightly alkaline reaction. Dishes thus platinised can be used with advantage for the evaporation of waters for analysis.—*Zeit. Anal. Chem.*, vol. xli., p. 618.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 17, October 26, 1903.

Fusibility of Mixtures of Sulphur and Bismuth.—H. Pélabon.—When the temperature of a mixture of sulphur and bismuth is gradually raised, the sulphur fuses first at about 114°, then the bismuth at about 255°. Finally, the two superposed liquids combine violently at 320°, with a development of heat enough to vaporise a portion of the sulphur. The author investigates the mixtures of varying proportions of sulphur and bismuth prepared in this manner. When a small proportion of sulphur is present there are usually two solidification-points. The final one is about 260°, *i.e.*, the fusing-point of bismuth. A curve of fusibility, having for abscissæ the proportion of sulphur in hundredths of the total weight of the mixture, and for ordinates the first solidification temperature, is shown in a diagram.

Action of Boric Acid on Iodides: its employment for the Separation of Iodine from Iodides in presence of Bromides and Chlorides.—H. Baubigny and P. Rivals.—Pure boric acid decomposes iodides in cold solution, giving HI, whilst it has no action (even when hot) on saturated solutions of bromides and chlorides. This property can be used for the separation of iodides from bromides and chlorides. If, therefore, an oxidising agent intervenes, the iodine can be liberated. Manganese dioxide, prepared artificially by the reduction of permanganate and washed, acts very well. It can be washed after desiccation at a low temperature (30—40°) in the form of a paste.

Heat of Combustion of Organic Acids, their Anhydrides and their Ether Salts.—P. Lemoult.—The author, by the aid of certain conventions which form the numerical basis of his calculations, evaluates the heat of combustion of all the organic compounds containing only carbon, hydrogen, and oxygen. In the 450 cases examined, there were 12 per cent where the approximation to the measured values is more than 1/100, 20 per cent where it varies between 1/100 and 1/200 of this value, and 68 per cent where it is less—and often considerably less—than 1/200th.

Researches on Isoglucosamine.—L. Maquenne.—Isoglucosamine, under the action of nascent hydrogen in alkaline solution, is converted into a mixture of two stereoisomeric bases belonging to the series of glucamines. The author identifies one of these as *d*-glucamine, properly speaking, the other as *d*-mannamine. This fact seems to confirm, in an indisputable manner, the existence of an α-ketonic function in the molecule of isoglucosamine, and shows that this base behaves towards reducing agents exactly in the same way as *d*-fructose. The author's experiments show that isoglucamine forms the basis of the new method of passing from the mannite to the sorbite series or *vice versâ*.

Action of Chlorine on Barium Acetate.—Albert Colson.—Lead acetate in acetic solution changes into chloride and plumbic tetracetate under the action of a current of chlorine. This reaction constitutes a simple method of verifying the tetravalency of an element, especially the constitution of O = Pb—O, lead dioxide. By applying the same reaction to barium, the author, up to the present time, has been unable to prepare a tetrabaric compound of the form BaX_4; barium remaining divalent, as if the dioxide corresponded to the constitution $Ba\begin{matrix}O\\|\\O\end{matrix}$.

Solid Azo-dyes derived from α-Aminoanthraquinone.—Charles Lauth.—The author investigates the question as to whether anthraquinonic compounds, which usually are solid, are capable of giving rise to the great family of azo-dyes, and if these azo-dyes resist physical and chemical agents. The preliminary experiments, in which he tried either to diazotise amidoalizarine or to join the hydroxyl-derivatives of anthraquinone with the diazoic compounds, were not successful. He then used as the starting basis α-amidoanthraquinone, which body is capable of being diazotised. He then successfully established that this diazo-compound combines with ordinary agents, and gives rise to rich solid dyes.

NOTES AND QUERIES.

, Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Electric Furnace.—Can any correspondent supply me with a description and probable cost of a small electric furnace for welding two small pieces of metals together? Probably a resistance coil attached to the town service, and the metals attached to the two poles and pressed together, would answer.—E. S. G.

MEETINGS FOR THE WEEK.

MONDAY, 30th.—Society of Arts, 8. (Cantor Lectures). "The Mining of Non-Metallic Minerals," by Bennett H. Brough.

WEDNESDAY, Dec. 2nd.—Society of Arts, 8. "The Fiscal Problem," by Sir Charles Malcolm Kennedy, K.C.M.G., C.B.

—— Society of Public Analysts, 8. "Characteristics of some Almond and Allied Oils," by J. Lewkowitsch, Ph.D., F.I.C. "Note on the Quantitative Estimation of Mechanical Wood Pulp in Papers," by C. F. Cross, F.I.C., and E. J. Bevan, F.I.C. "Estimation of Aldehydes and Ketones in Essential Oils," by H. E. Burgess. "Note on the Examination of Sperm Oil," by L. Myddleton Nash, F.I.C.

THURSDAY, 3rd.—Chemical, 8. "Molecular Formulæ of some Fused Salts as determined by their Molecular Surface Energy," by J. F. Bottomley. "Acid Salts of Monobasic Acids," by R. C. Farmer. "Atmospheric Corrosion of Zinc," by G. T. Moody. "Solubilities of the Hydrates of Nickel Sulphate," by B. D. Steele and F. M. G. Johnson.

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PHYSICS	A. GRIFFITHS, D.Sc.
MATHEMATICS	E. H. SMART, M.A.
BOTANY	A. B. RENDLE, M.A., D.Sc.
ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
GEOLOGY & MINERALOGY	G. F. HARRIS, F.G.S.
METALLURGY, MINING, and ASSAYING ..	G. PATCHIN, A.R.S.M.

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2297.

RADIO-ACTIVE SUBSTANCES.*

By Mdme. SKLODOWSKA CURIE.

(Concluded from p. 261).

Chapter IV. (*continued*).

Theory of Interpretation of the Causes of Variations of Activity of Radium Salts after Solution and after Heating.

The facts previously indicated may be in part explained by the theory according to which the energy of radium is produced in the form of an emanation, which is then transformed into the energy of radiation. When a radium salt is dissolved, the emanation produced by it spreads beyond the solution, and causes radio-activity outside the source from which it proceeds; when the solution s evaporated, the solid salt obtained is but slightly active, because it contains only a small amount of emanation. Gradually the emanation is accumulated in the salt, the activity of which rises to a limiting value, which is reached when the production of the emanation by the radium compensates the loss by external emission and by local transformation into Becquerel rays.

When a radium salt is heated, the external emission of the emanation is greatly increased, and the phenomena of induced radio-activity are more intense than when the salt is at the ordinary temperature. But when the salt returns to the ordinary temperature it is exhausted, as is the case after being dissolved, and contains but a small amount of emanation, its activity having become greatly reduced. Gradually the emanation accumulates afresh in the solid salt, and the radiation increases.

It may be said that radium gives rise to a constant generation of an emanation—part of which escapes to the exterior, the remainder being transformed in the radium itself into Becquerel rays. When radium is raised to a red heat, it loses the greater part of its capacity to cause the induction of activity; otherwise stated, the evolution of the emanation is lessened. Consequently, the proportion of the emanation utilised in the radium itself should be greater, and the substance attains a higher limit of radio-activity.

We will endeavour to establish theoretically the law of rise of activity of a solid radium salt which has been dissolved or has been heated. We will assume that the intensity of radiation of radium is, at each instant, proportional to the quantity of emanation, q, present in the radium. We know that the emanation is spontaneously destroyed according to a law such that, at each instant,—

$$q = q_0 e^{-\frac{t}{\theta}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 1,$$

q_0 being the amount of the emanation at the moment of starting the observation, and θ the time constant, equal to $4{\cdot}97 \times 10^5$ secs.

Now let Δ be the evolution of the emanation by radium, a quantity which I will assume constant. Let us consider what would occur if no emanation were escaping to the exterior. The emanation generated would then be completely utilised by the radium for the production of the radiation. We have from Formula 1—

$$\frac{dq}{dt} = -\frac{q_0}{\theta} e^{-\frac{t}{\theta}} = -\frac{q}{\theta};$$

and consequently, in the state of equilibrium, the radium would contain a certain quantity of emanation, Q, such that—

$$\Delta = \frac{Q}{\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 2,$$

and the radiation of the radium would then be proportional to Q.

Let us suppose the radium placed in the circumstances under which it gives off the emanation to the exterior; this is obtained by dissolving the radium compound or by heating it. The equilibrium will be disturbed, and the activity of the radium diminished. But as soon as the cause of the loss of emanation has been abolished (the body being restored to the solid state or the heating having ceased), the emanation is accumulated afresh in the radium and we have a period during which the evolution, Δ, surpasses the velocity of destruction, $\frac{q}{\theta}$. We then have—

$$\frac{dq}{dt} = \Delta - \frac{q}{\theta} = \frac{Q-q}{\theta},$$

from which—

$$\frac{d}{dt}(Q-q) = -\frac{Q-q}{\theta},$$

$$Q - q = (Q - q_0) e^{-\frac{t}{\theta}} \quad . \quad . \quad . \quad . \quad . \quad 3,$$

q_0 being the amount of emanation present in the radium at time $t = 0$.

According to Formula 3, the excess of the quantity of emanation, Q, contained by the radium in a state of equilibrium above the quantity, q, contained at a given moment, decreases as a function of the time according to an exponential law, which is also the law of the spontaneous disappearance of the emanation. The radiation of radium being proportional to the amount of emanation, the excess of the intensity of the limiting radiation above the actual intensity should decrease as a function of the time by the same law; the excess should thus diminish to one-half in about four days.

The preceding theory is incomplete, since the loss of emanation to the exterior has been neglected. It is also difficult to determine the manner in which this acts as a function of the time. In comparing the results of experiment with those of this incomplete theory, there is found to be no satisfactory agreement; the conviction is, however, retained that the theory in question is partially true. The law by which the excess of limiting activity above the actual activity diminishes to one-half in four days represents approximately the course of the renewal of activity after heating for ten days. In the case of the renewal of activity after solution, the same law appears to hold approximately for a certain period of time, which begins two or three days after evaporation to dryness and continues for ten or fifteen days. The phenomena are otherwise complex; the theory sketched out does not explain the reason of the suppression of the penetrating rays in greater proportion than the absorbable rays.

Nature and Cause of the Phenomena of Radio-activity.

From the beginning of research upon the radio-active bodies, and when the properties of these bodies were yet hardly known, the spontaneity of their radiation presented itself as a problem having the greatest interest for physicists. To-day we have advanced considerably in the understanding of radio-active bodies, and are able to isolate one of very great power, viz., radium. With the object of making use of the remarkable properties of radium, a profound investigation of the rays emitted by radio-active bodies is indispensable; the various groups of rays under investigation present points of similarity with the groups of rays existing in Crookes tubes: cathode rays, Rontgen rays, canal rays. The same groups of rays are found in

* Thesis presented to the Faculté des Sciences de Paris.

the secondary radiation produced by Röntgen rays, and in the radiation of bodies which have acquired radio-activity by induction.

But if the nature of the radiation is actually better known, the cause of this spontaneous radiation remains a mystery, and the phenomena always presents itself to us as a profound and wonderful enigma.

The spontaneously radio-active bodies, and in the first place radium, are sources of energy. The evolution of energy, to which they give rise, is manifested by Becquerel radiation, by chemical and luminous effects, and by the continuous generation of heat.

The question often arises as to whether energy is created within the radio-active bodies themselves, or whether it is borrowed by them from external sources. No one of the numerous hypotheses arising from these two points of view has yet received experimental confirmation.

The radio-active energy may be assumed to have been initially accumulated and then gradually dissipated, as happens in the case of long continued phosphorescence. We may imagine the evolution of radio-active energy to correspond to a transformation of the nature of the atom of the active body; the fact of the continuous generation of heat by radium speaks in favour of this hypothesis. The transformation may be assumed to be accompanied by a loss of weight and by an emission of material particles constituting the radiation. The source of energy may yet be sought in the energy of gravitation. Finally, we may imagine that space is constantly traversed by radiations yet unknown, which are arrested in their course by radio-active bodies and transformed into radio-active energy.

Many reasons are adduced for and against these different views, and most often attempts at experimental verifications of the conclusions drawn from these hypotheses have given negative results. The radio-active energy of uranium and radium apparently neither becomes exhausted nor varies appreciably with lapse of time. Demarçay examined spectroscopically a specimen of pure radium chloride after a five months' interval, and observed no change in the spectrum. The principal barium line, which was visible in the spectrum, indicating the presence of a trace of barium, had not increased in intensity during the interval, showing therefore that there was no transformation of radium into barium to an appreciable extent.

The variations of weight announced by M. Heydweiller in radium compounds cannot yet be looked upon as established facts.

Elster and Geitel found that the radio-activity of uranium is not affected at the bottom of a mine-shaft 850 m. deep; a layer of earth of this thickness would therefore not affect the hypothetical primary radiation which would be excited by the radio-activity of uranium.

We have determined the radio-activity of uranium at midday and at midnight, thinking that if the hypothetical primary radiation had its origin in the sun it would be partly absorbed in traversing the earth. The experiment showed no difference in the two determinations.

Conclusions.

I will define, in conclusion, the part I have personally taken in the researches upon radio-active bodies.

I have investigated the radio-activity of uranium compounds. I have examined other bodies for the existence of radio-activity, and found the property to be possessed by thorium compounds. I have made clear the atomic character of the radio-activity of the compounds of uranium and thorium.

I have conducted a research upon radio-active substances other than uranium and thorium. To this end I investigated a large number of substances by an accurate electrometric method, and I discovered that certain minerals possess activity which is not to be accounted for by their content of uranium and thorium.

From this I concluded that these minerals must contain a radio-active body different from uranium and thorium, and more strongly radio-active than the latter metals.

In conjunction with M. Curie, and subsequently with MM. Curie and Bémont, I was able to extract from pitch-blende two strongly radio-active bodies—polonium and radium.

I have been continuously engaged upon the chemical examination and preparation of these substances. I effected the fractionations necessary to the concentration of radium, and I succeeded in isolating pure radium chloride. Concurrently with this work, I made several atomic weight determinations with a very small quantity of material, and was finally able to determine the atomic weight of radium with a very fair degree of accuracy. The work has proved *that radium is a new chemical element.* Thus the new method of investigating new chemical elements, established by M. Curie and myself, based upon radio-activity, is fully justified.

I have investigated the law of absorption of polonium rays, and of the absorbable rays of radium, and have demonstrated that this law of absorption is peculiar and different from the known laws of other radiations.

I have investigated the variation of activity of radium salts, the effect of solution and of heating, and the renewal of activity with time, after solution or after heating.

In conjunction with M. Curie, I have examined different effects produced by the new radio-active substances (electric, photographic, fluorescent, luminous, colourations, &c.).

In conjunction with M. Curie, I have established the fact that radium gives rise to rays charged with negative electricity.

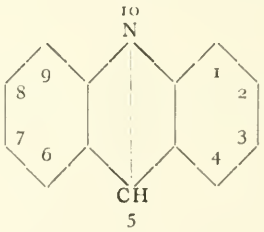
Our researches upon the new radio-active bodies have given rise to a scientific movement, and have been the starting-point of numerous researches in connection with new radio-active substances, and with the investigation of the radiation of the known radio-active bodies.

ON ACRIDINES.*

By ALFRED SENIER, Ph.D.,
Professor of Chemistry in Queen's College, Galway.

I. *Discovery and Constitution.*

In 1871 Graebe and Caro (*Annalen*, 1871, clviii., 265) isolated from crude anthracene a yellow crystalline base which, on account of its irritating action on the skin and mucous membranes, was named Acridine. The base exhibits in solution a beautiful blue fluorescence. Salts, alkhalides, a dihydride, and a compound with iodine are described; also, as the result of oxidation, a ketonic derivative and a dibasic (acridinic) acid. The well-known researches of Graebe (*Ber.*, 1872, v., 15; 1880, xiii., 99) which followed, and especially those of Riedel (*Ber.*, 1883, xvi., 1609), showing the relation of acridinic acid to quinoline, established the constitution of acridine which is now accepted:—



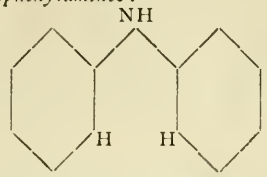
The resources of synthetical chemistry were not long in bringing to light methods for building this interesting fluorsphoric molecule from known compounds of simpler structure. In 1882 Bernthsen (*Ber.*, 1882, xv., 3011; 1883, xvi., 767) obtained a phenyl derivative, and Bernthsen and

* Abstract of a Paper read before the British Association (Section B), Southport Meeting, 1903.

O. Fischer (*Ber.*, 1883, xvi., 68) an analogous methylacridine. The base itself soon afterwards yielded to the endeavours of Bernthsen and Bender (*Ber.*, 1883, xvi., 1802), resulting from the condensation of diphenylamine and formaldehyde.

II. *Methods of Formation.*

1. *From Diphenylamines :—*



i. With benzonitrile (Bernthsen, *Ber.*, 1882, xv., 3011 ; 1883, xvi., 767).

ii. With formaldehyde and other aldehydes.
Bernthsen and Bender, *Ber.*, 1883, xvi., 1802.
Besthorn and Curtmann, *Ber.*, 1891, xxiv., 2039.
Casella, German Patent 120466.
Ullmann, *Ber.*, 1903, xxxvi., 1017.
Also—
Möhlau, *Ber.*, 1886, xix., 2451.
Eliasberg and Friedländer, *Ber.*, 1892, xxv., 1752.

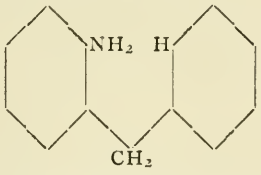
iii. With acetic and other acids.
Besthorn and O. Fischer, *Ber.*, 1883, xvi., 68.
Bernthsen and Traube, *Ber.*, 1884, xvii., 1508.
Hess and Bernthsen, *Ber.*, 1885, xviii., 689.
Bonna, *Annalen*, 1887, ccxxxix., 55.
Besthorn and Curtmann, *Ber.*, 1891, xxiv., 2039.
Volpi, *Gazzetta*, 1891, xxi., [2], 228 ; 1892, xxii., [2], 549.

iv. With chloroform (O. Fischer and Körner, *Ber.*, 1884, xvii., 101).

v. With methylene di-iodide (Senier and Goodwin, *Journ. Chem. Soc.*, 1902, lxxxi., 280).

vi. An *o*-methyl derivative led through red-hot tube (Graebe, *Ber.*, 1884, xvii., 1370).

2. *From Diphenylmethanes :—*



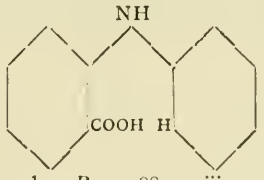
i. *o*-Amino-diphenylmethane oxidised.
O. Fischer and Schütte, *Ber.*, 1893, xxvi., 3085.
Also—
German Patent 118075.
Haase, *Ber.*, 1903, xxxvi., 591.
Ullmann, *Ber.*, 1903, xxxvi., 1017.

III. *Acridones and Thioacridones.*

1. *Methods of Formation :—*

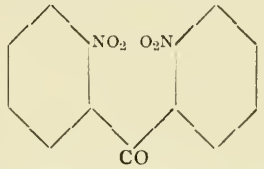
i. From acridine by direct oxidation or sulphurisation.
Graebe and Caro, *Ber.*, 1880, xiii., 99.
Graebe and Lagodzinski, *Annalen*, 1893, cclxxvi., 35.
Decker, *Journ. Prakt. Chem.*, 1892, [2], xlv., 161.
Edinger, *Ber.*, 1900, xxxiii., 3769.
Edinger and Arnold, *Journ. Prakt. Chem.*, 1901, [2], lxiv., 182 and 471.
German Patent 120586.

ii. From derivatives of diphenylamine-*o*-carboxylic acid :—



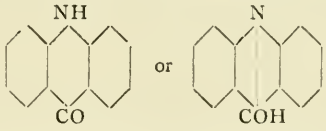
Jourdan, *Ber.*, 1885, xviii., 1444.
Graebe and Lagodzinski, *Ber.*, 1892, xxv., 1733.
Schöpff, *Ber.*, 1892, xxv., 1980.
Graebe and students, *Annalen*, 1894, cclxxix., 268.

iii. From derivatives of dinitro- or diamino-diphenyl ketones, for example :—



Schöpff, *Ber.*, 1894, xxvii., 2316.
Staedel, *Ber.*, 1894, xxvii., 3362.

2. *Constitution.* — Of the two formulæ, ketonic or hydroxyl, which have been suggested for acridones.—



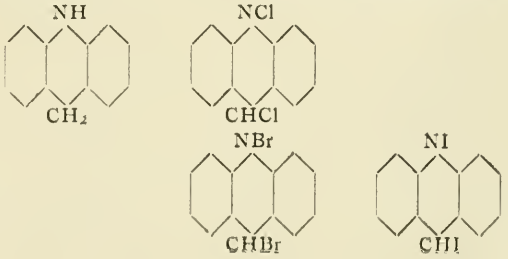
the ketonic best explains the synthesis from phenones ; but the acridones exhibit fluorescence, which indicates rather the *para* linking of the hydroxyl formula. The behaviour of thioacridone towards phosphorus pentachloride is also in favour of the latter view. Jourdan, in 1885, described two isomeric acridones : one showing fluorescence, to which he ascribed the hydroxyl formula ; the other, not possessing that property, which he believed to have the ketonic structure. Possibly the acridones are an instance of tautomerism, and are certainly worthy of further inquiry.

IV. *Dihydrides, Dihalides, Salts, and Alkhalides.*

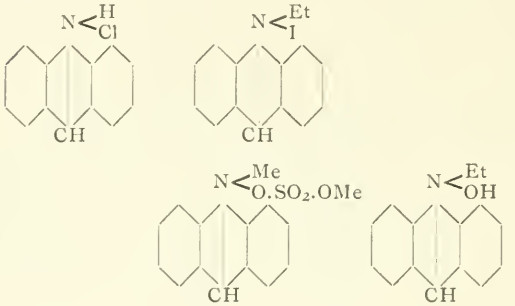
Unstable dihydrides of acridines (hydroacridines) have been isolated in many instances, especially in the case of naphthacridines. The first compound of this class is described by Graebe and Caro in their first paper.

In conjunction with Mr. Goodwin I have prepared similar dihalides. We have isolated dichlorides, dibromides, and diiodides of acridine, of our hexamethylacridine, of Reed's naphthacridine, and of our naphthacridine. These compounds form beautiful crystals, but gradually decompose in solution. This inquiry is not yet completed.

Neither of these classes of compounds appear to show fluorescence, and it seems best to give to them the formula corresponding to that originally proposed by Bernthsen and Bender (*Ber.*, 1883, xvi., 1971) for the "hydroacridines" :—



Acridine salts and alkhalides show fluorescence when in solution, and, following Bernthsen and Bender (*Ber.*, 1883, xvi., 1802), they are best regarded as acridinium salts thus :—



(To be continued).

PURIFICATION AND ESTIMATION OF IODINE.

By ABRAHAM GROSS.

In view of the importance of iodine in the arts and of the apparent difficulty in obtaining it absolutely pure, a discussion of this subject does not appear untimely, and may prove of some value. Very few methods have been published in the direction of iodine purification, and but one finds favourable mention.

This is the method used by Stas in his researches on the atomic weight of iodine, and consists in dissolving iodine in a solution of potassium iodide, precipitating the iodine with water, drying over calcium nitrate, and subliming the dried mass.

This method is criticised by Lean and Whatmough (*Journ. Chem. Soc.*, 1899), who state that pure iodine can be obtained by heating cuprous iodide in dried air at 240° C., when the iodine is liberated.

Other investigations on this subject have been made by C. Meineke (*Chem. Zeit.*, xvi., p. 1219) and Z. Musset (*Zeit. fur Anal. Chem.*, 1901, p. 45).

With desire to obtain a reliable method for purifying iodine it was considered advisable to test the efficacy of the Stas method, and to compare the purity of the iodine thus produced with that obtained by other methods which suggested themselves at the time.

Accordingly, the following scheme was planned :—

1. The Stas method.

2. Washing iodine with water, drying a portion over sulphuric acid, another portion over calcium nitrate, and a third portion over calcium chloride.

3. Mixing iodine with potassium iodide, and drying over sulphuric acid.

Each of the above was then sublimed three times after drying.

The first method was carried out according to the directions of Stas, who states that to dissolve 4 kilos. of iodine a solution of 1 kilo. of potassium iodide in 1 kilo. of water was required.

These proportions were found inadequate, for after standing some time, with frequent shaking, a considerable portion of the iodine remained undissolved.

Several additions of potassium iodide and water were made until complete solution was effected. This was accomplished when the proportions were four of iodine to two of potassium iodide and two of water.

The solution of iodine was then poured into water and allowed to stand until all of the iodine was precipitated. The supernatant fluid was poured off, the iodine washed with water until free from potassium iodide. It was then brought upon a filter with sand as a filtering medium, and the water withdrawn by suction. The iodine was then transferred to a shallow dish, and dried over calcium nitrate, which was replaced as soon as effected by the moisture. The drying continued twelve days. The dried sample was then sublimed three times by a process which will be described later.

In the next three methods, the iodine was washed with water fifteen times, and, after as much water as possible had been withdrawn by suction, was divided into three portions, and dried as previously mentioned over sulphuric acid, calcium nitrate, and calcium chloride respectively.

In conducting this experiment two other points were in view :—

A. To determine the best drying agent.

B. To ascertain whether any chlorine would be set free and absorbed by the iodine when the sample was dried over calcium chloride.

It may be mentioned here that the calcium nitrate and sulphuric acid were equally efficient as drying agents, but the inconvenience of constantly changing the calcium nitrate rendered it less desirable.

Each of these samples was then sublimed three times.

The fifth sample was prepared by mixing iodine with pure potassium iodide, drying over sulphuric acid, and subliming three times.

The iodine obtained by this method was discarded, as a white residue remained after each sublimation.

Apparently the potassium iodide was carried over with the iodine vapour.

Process of Sublimation.

The iodine prepared by the methods previously described was placed in a piece of combustion tubing slightly inclined, and resting on a support. Following the iodine was a plug of ignited asbestos to prevent the heated iodine from running down the tube. The lower end of the tube was connected to two tubes containing phosphoric anhydride, and one containing calcium chloride. In this manner the air drawn through was perfectly dry. The upper end was covered by a bottle fitted to a rubber cork to catch any vapour not previously condensed.

Through the cork passed a glass tube which connected to an empty jar as a precautionary measure, and in turn to a cylinder containing water and the suction pump. The suction was regulated by the bubbles produced in the cylinder. To prevent any accident from too sudden heating a piece of iron pipe was placed over that part of the tube containing the asbestos and iodine, and extending beyond for about four inches. This was protected from the glass by asbestos.

A gentle heat was used and enough suction applied to condense the vapour sufficiently far enough away from the pipe to prevent any liquefaction of the sublimed crystals.

The succeeding two sublimations were conducted in precisely the same manner.

The following method proved itself highly satisfactory in the determination of the purity of iodine.

About 2 grms. of the iodine were placed in a flask, 40 c.c. of water, and about 4 grms. of shot zinc added.

The flask was then shaken, and allowed to stand with stopper inserted until the fluid was colourless. When all the iodine was taken up by the zinc the solution was filtered into a half litre flask, the residue and zinc hydrate washed with hot water until free from iodine, and the fluid made up to 500 c.c.

Fifty c.c. of the solution was placed in a porcelain dish and titrated with silver nitrate, using potassium chromate as an indicator until the end point, a slight brownish colour, was reached.

The following results were obtained :—

Stas Method.—Mean of five determinations gave 100·02 per cent.

Second Method.—Mean of five determinations gave ·65 per cent.

A sample of unpurified iodine gave, by this method, 98·83 per cent.

The iodine dried over the calcium chloride was tested for chlorine according to Fresenius ("Qual. Analysis"), but none was found.

For comparison a sample of unpurified iodine was tested by the same method, and the presence of the chlorine was indicated.

The following summary may be deduced from the foregoing research:—

1. The Stas method gave the purest iodine.
2. Sulphuric acid was the best drying agent.
3. The iodine was not contaminated when dried over calcium chloride.
4. The iodine, when pure, was satisfactorily determined when converted into zinc iodide, and titrated with silver nitrate, with potassium chromate as an indicator.—*Proceedings of Engineers' Society of Western Pennsylvania*, xix., No. 6.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, November 5th, 1903.

Prof. Tilden, D.Sc., F.R.S., President, in the Chair.

(Concluded from p. 269).

137. "*Note on some Reactions of Vanadium Tetrachloride.*" By B. D. Steele.

In a series of experiments undertaken with the object of ascertaining whether vanadium tetrachloride might not find useful application as a chlorinating and condensing agent, it was found that on adding this reagent to benzene, a small quantity of a dark mauve solid was precipitated, the yield of this substance was much increased by boiling the mixture, and 13 grms. of dried solid were obtained from 25 grms. of benzene and 15 grms. of vanadium tetrachloride. Analyses showed that the atomic ratio of chlorine to vanadium varied from 3·08 to 2·73, whilst that between carbon and hydrogen was found to be one. The substance rapidly decreased in weight at the ordinary temperature, and a freshly prepared sample, when heated at 100°, evolved benzene, and diminished by 50 per cent, the calculated percentage loss in weight for the compound $VCl_3(C_6H_6)_2$ being 49·7. In the above reaction, the vanadium tetrachloride was reduced to trichloride, and the liberated chlorine atom attacked the benzene molecule, evolving hydrogen chloride and giving rise to chlorobenzene or some other more highly chlorinated substitution products of benzene.

Vanadium tetrachloride failed entirely to bring about chlorination in the case of nitrobenzene, but was used successfully in chlorinating benzene.

When a rapid current of chlorine was passed into a mixture of 4·5 grms. of the chloride and 100 grms. of benzene, hydrochloric acid was copiously evolved, and sufficient heat was developed to raise the temperature of the solution nearly to its boiling-point. On fractionating the product after removal of the vanadium compounds, a considerable quantity of substance boiling between 128° and 132° was obtained, which was identified as chlorobenzene. Crystals of hexachlorobenzene melting at 155° were isolated from the small residue left in the distilling flask.

Vanadium tetrachloride has no value as a condensing agent for use in the laboratory. Acetyl chloride and benzene, when condensed in its presence, gave only a very small yield of acetophenone, and other experiments in this direction led to equally unfavourable results.

It was found that when the mauve compound, $VCl_3(C_6H_6)_2$, reacted with ether, heat was developed, and a blue solution was produced which, on evaporation over sulphuric acid in a desiccator, yielded fine, blue, tabular crystals; these could only be kept in the presence of an excess of ether and in a dry atmosphere. Satisfactory analyses of this compound could not be made on account of its instability.

138. "*Studies on Comparative Cryoscopy.* Part I. *The Fatty Acids and their Derivatives in Phenol Solution.*" By P. W. Robertson.

The rate of association of a given compound in any solvent is termed the "assoce," and the constant has been determined for the fatty acids and their derivatives in phenol solution.

The assoce of the normal fatty acids alternately rises and falls as the series is ascended. If the even members are considered, this coefficient reaches a minimum at hexoic acid, and then rises rapidly. It is shown that the subsequent rise is probably due to a different kind of association, inasmuch as it is caused by the hydrocarbon portion of the molecule.

The assoce is influenced both by the nature and by the position of a substituting group, and, generally, halogens, alkyl radicles of low molecular weight, and phenyl and benzyl groups have the same influence. In all cases, when these radicles are introduced into the α-position with respect to the carboxyl group the assoce is reduced, but in the other non-contiguous positions they have little or no effect.

Dicarboxylic acids associate more rapidly than the acids from which they are derived, but here again replacement of the α-hydrogen atoms causes a reduction in the rate of association. α-Hydroxyl radicles increase the assoce, but substituted amino-groups tend to change its sign. It is noteworthy that the di- and tri-carboxylic acids and the α-amino-acids are exceeding insoluble in phenol.

The rates of association of the substituted acetic acids are intimately connected with their velocities of etherification.

139. "*Vapour Pressures of Sulphuric Acid Solutions.*" Preliminary Note. By B. C. Burt.

Regnault's determinations of the vapour pressure of sulphuric acid solutions were carried out for concentrations varying from 24 to 84 per cent at temperatures ranging from 5° to 30°. The vapour pressures are now being determined through wider limits of temperature and concentration by means of a modified form of the apparatus described by Innes (*Trans.*, 1902, lxxxi., 683).

The sulphuric acid solutions are heated in a large Jena glass Beckmann tube, having a stout platinum wire sealed through the bottom. Regular ebullition is ensured by the use of small glass beads, and the tube is kept at a constant temperature by a copper jacket containing a suitable liquid boiling under a known pressure.

The experimental tube is connected to a large reservoir, the pressure of which is kept constant by means of the regulator described by Innes. By suitably adjusting the pressure, which is observed to 0·1 m.m. by a mercury manometer, the sulphuric acid can be boiled at any required temperature, this being read off by special normal Jena glass mercury thermometers (Goetz).

The appended results indicate the accuracy of the method:—

Series A.

Concentration of acid in percentages.	Temperature.	Vapour pressure in m.m.
54·70	131°	637·1
54·70	131	637·2
62·07	131	497·9
62·07	131	497·7
62·07	131	497·7
72·88	132	200·2
72·88	132	200·3
79·57	132·5	70·2
79·57	132·5	70·2

Series B.

Concentration of acid in percentages.	Temperature.	Vapour pressure in m.m.
72·88	157	421·6
72·88	157	421·5
79·57	157	182·4
79·57	157	182·2

Chlorobenzene was used as the boiling liquid in Series A, and bromobenzene in Series B.

140. "*Additive Compounds of* s-*Trinitrobenzene and Alkylated Arylamines.*" By H. Hibbert and J. J. Sudborough.

Mono- and di-alkylated naphthylamines form definite additive compounds with *s*-trinitrobenzene which closely resemble the similar products obtained from α- and β-naphthylamines and the same trinitro-compound. They are stable, red or purplish-black, crystalline substances, and may be crystallised from all the ordinary solvents, including glacial acetic acid, without being resolved into their components, but are readily decomposed by hot dilute mineral acids.

Molecular weight determinations in dilute benzene solution indicate that the dissolved compounds are almost completely resolved into their components.

Most of the monoalkylated derivatives, like the compounds from α- and β-naphthylamines, may be acetylated, whereas the additive compounds from the tertiary bases may be boiled with acetic anhydride for hours without undergoing change.

A *benzoyl* derivative has been obtained by the action of benzoyl chloride and alkali hydroxides on α-naphthylamine trinitrobenzene; it melts at 131—132°, and is identical with the compound formed by the union of benzo-α-naphthalide and *s*-trinitrobenzene. *Ethyl-α-naphthylamine* s-*trinitrobenzene* melts at 153·5—154° and the corresponding *diethyl* compound at 95—95·5°. *Dimethyl-α-naphthylamine* s-*trinitrobenzene* melts at 105—106° and *ethyl-β-naphthylamine* s-*trinitrobenzene at* 106°, *ethylaceto-β-naphthalide* s-*trinitrobenzene* and *diethyl-β-naphthylamine* s-*trinitrobenzene* melt at 77—78° and 116° respectively.

Mono- and di-alkylated anilines also combine with *s*-trinitrobenzene, but the products are extremely unstable, and when crystallised from any of the ordinary solvents, or when exposed to the air at the ordinary temperature, are readily decomposed into their components.

141. "*Interaction between Chloric and Hydriodic Acids.*" By J. McCrae.

The action of chloric acid on hydriodic acid is known to take place according to the equation $6H' + ClO_3' + 6I' = 3I_2 + Cl + 3H_2O$, and its velocity has been studied by the compensation method by Bray (*Journ. Phys. Chem.*, 1903, vii., 92). Some experiments on this subject had been carried out prior to the publication of Bray's work, but as they only confirmed these results, the work has been discontinued.

The method at first adopted was to mix definite volumes of standard solutions of potassium chlorate and potassium iodide and add a known volume of N sulphuric acid, so that the concentrations were accurately known. When no acid is added, iodine is not separated, even after twelve months, when the solution is allowed to remain at the ordinary temperature and exposed to daylight. The velocity of the reaction is dependent on the concentration of hydrogen ions, and the reaction is an extremely suitable one for demonstrating the velocity of reaction. If 10 c.c. of 0·2 N potassium chlorate solution, 60 c.c. of 0·2 N potassium iodide solution, and 15 c.c. of N sulphuric acid are mixed, the solution remains almost colourless for a few minutes; a little of the mixture may then be warmed to show that the velocity is accelerated by rise of temperature. In the course of some hours, the intensity of the colouration increases perceptibily, but it is only after six or seven weeks that the maximum reaction has taken place at the ordinary temperature. After definite intervals of time, portions of the solution were titrated with N/100 sodium thiosulphate solution, and the velocity of reaction calculated in the ordinary way.

During the course of some experiments with excess of potassium chlorate, it was observed that the concentration of the iodine in solution rose to a maximum and then diminished; at the same time, much iodine had volatilised on to the cork of the flask containing the solution. The same experiment was then made in a glass-stoppered bottle. The maximum intensity of colouration in this case was apparently reached in about six weeks, and soon after iodine began to crystallise out. After about eleven or twelve weeks, the solution was quite colourless, and some very well-developed crystals of iodine were found in the bottle. About two months after the solution had become colourless, the iodine crystals had completely disappeared. As there was still the chance of leakage, the same experiment was carried out in a sealed tube. Five c.c. of N/5 potassium iodine solution, 45 c.c. of N/5 potassium chlorate solution, and 15 c.c. of N sulphuric acid were sealed in a wide glass tube, which was then freely exposed to the light. So far as could be judged by the eye, the maximum intensity of colouration was reached in about twenty-four days, and on the twenty-seventh day crystals of iodine began to separate. The colour of the solution then began to diminish in intensity, and after about fifty days the colour disappeared completely and the quantity of iodine separated was considerable. The iodine then began to dissolve slowly, and after about five months (from the beginning of the experiment) the whole of the iodine passed completely into solution without imparting any colour to the solution; during the period in which this dissolution was taking place, it was frequently noticed that in proximity with each iodine crystal, a yellow solution was formed, as if the iodine were being dissolved *per se*.

These results suggest that the reaction proceeds further than is denoted by the above equation, and they do not suggest in any way that a definite equilibrium is established.

Saturated solutions of potassium chlorate were sealed in tubes (1) with a small amount of iodine, and (2) with a large excess of iodine. In both cases, the iodine dissolved and the solution became yellow; the intensity of colouration appeared to increase progressively to a maximum after several days, and after four months there is no perceptible evidence of any diminution of the colouration. The fact that the colour only slowly developed shows that it is not due simply to physical dissolution of the iodine in the potassium chlorate solution, but suggests that a chemical reaction has taken place whereby potassium iodide or iodine ions have been formed, which then cause the iodine to pass into solution. As no acid was used in these cases, it is at present not possible to see what bearing the results have on the previous case, where the reaction takes place in presence of acid.

142. "3 : 5-*Dichloro*-1 : 1 : 2-*trimethyl*-Δ^2 : 4-*dihydro benzene*." A Correction. By A. W. Crossley.

Some time ago (*Trans.*, 1901, lxxix., 144), the author described a substance obtained by the action of phosphorus pentachloride on trimethyldihydroresorcin as 3 : 5-dichloro 1 : 1 : 2-trimethyl-Δ^2 : 4-dihydrobenzene (Δ^2 : 6-dichloro-3 : 4 : 4-trimethyldihydrobenzene),—

$$CMe_2 < \begin{matrix} CMe : CCl \\ CH_2—CCl \end{matrix} \geqq CH.$$

On further examination, this compound has been shown to be an aromatic substance, and is in reality a *dichlorotrimethylbenzene*. At the time the work was done, it was not known that phosphorus haloids acted on dihydroresorcins to give aromatic derivatives; the fact has only since been established (*Trans.*, 1902, lxxxi., 1536; 1903, lxxxiii., 116, 502); moreover, as the formulæ of these two substances differ only by two hydrogen atoms, analysis is not of much help in deciding between them.

Dichlorotrimethyldihydrobenzene is produced during the action of phosphorus pentachloride on trimethyldihydro-

resorcin (*loc. cit.*), and is contained in the liquid boiling at 120—125° under 31 m.m. pressure.

The chemical properties of both these substances will be described in detail on a future occasion.

143. "*The Estimation of Hydroxylamine.*" By H. O. Jones and F. W. Carpenter.

The methods hitherto described for the estimation of hydroxylamine were found to be very untrustworthy in the presence of substances such as neutral metallic salts, although these compounds would not be expected to affect the reactions involved. The following process has been devised, which is free from these objections, and is simple and accurate.

Ten to 20 c.c. of the hydroxylamine solution (which should not contain more than 0·5 per cent of the base) are added to a hot solution of copper potassium carbonate or copper potassium tartrate, which is well stirred during the addition. The mixture is raised to the boiling-point, the cuprous oxide at once collected in a Gooch crucible, washed with hot water, and dissolved in ferric sulphate solution in an atmosphere of carbon dioxide, the ferrous salt produced being titrated with potassium permanganate solution as recommended by Wood and Berry (*Proc. Camb. Phil. Soc.*, 1903, xii., [2], 97). Four mols. of the permanganate correspond with 10 mols. of hydroxylamine.

The foregoing reactions are not affected by the presence of foreign substances provided that these do not reduce the copper solutions, and the method may be applied to mixtures containing sodium, potassium, ammonia, cobalt, nickel, and zinc salts, carbon dioxide, alcohol, acetic acid, and ketoximes.

144. "*A Study of the Isomerism and Optical Activity of Quinquevalent Nitrogen Compounds.*" By H. O. Jones.

An attempt has been made to prepare isomerides of quaternary ammonium compounds of the type $N{\cdot}R\,R'\,R_2''\,X$. The existence of these isomerides is theoretically possible on any configuration of the nitrogen atom, since it has been proved conclusively by the work of Pope and his colleagues that the configuration of radicles about a quinquevalent nitrogen atom is a stable one giving rise to optical activity. Taking Bischoff's "pyramidal" configuration, which affords the best explanation of the facts at present known, two isomerides are to be expected, one of which should be capable of existing in optically active forms.

Seven compounds of the desired type have been produced (with one exception in two different ways) and their properties studied, but no evidence of isomerism was obtained. The compounds have been examined for optical activity by the fractional crystallisation of the *d*-camphorsulphonate and the *d*-bromocamphorsulphonate from non-hydroxylic solvents; in no case was any resolution effected, so that the compound produced in all cases have a planisymmetric configuration. The absence of isomerism is discussed in the light of Kipping's results on the isomerism of compounds of the type NRH_3X, in which R and X both contain an asymmetric carbon atom.

Optical activity due to an asymmetric nitrogen atom is to be expected in α- and β-substituted pyridinium compounds and in certain tetrahydroquinolinium derivatives. Several of these compounds have been examined by the method already mentioned, but for some unknown reason no resolution could be effected.

d-*Phenylbenzylmethylethylammonium* d-*camphorsulphonate* melts at 181° and the corresponding d-*iodide* at 146—147°; the *platinichloride* of *d*-phenylmethylethylallylammonium *d*-bromocamphorsulphonate melts at 159—160°.

145. "*The Influence of Various Substituents on the Optical Activity of Tartramide.*" By P. F. Frankland and A. Slator.

This paper forms a part of the systematic investigation being made by one of the authors on the connection between the rotation and chemical constitution of optically active molecules. The preparation and properties of seventeen derivatives of tartramide are described, the series including the methyl, ethyl, and benzyl amides, the anilide toluidides (*o*-, *m*-, and *p*-), and α- and β-naphthylamides; the anil and *p*-toluil; the hydrazide and phenylhydrazide; the hydrazones of benzaldehyde, furfuraldehyde, and acetophenone; as well as the *o*-toluidide of diacetyltartaric acid.

In order to avoid errors arising from the possible racemisation of the tartaric acid, the compounds have, in nearly all cases, been prepared by the direct interaction of acid and base, as well as by acting with the base on an ethereal salt of the acid; but, although the latter reaction could generally be made to take place at a lower temperature than the former, no substantial difference in the optical activity of the products was discoverable.

All the compounds were, like tartramide itself, dextrorotatory. The molecular rotation is considerably increased by the introduction of the methyl, ethyl, and benzyl groups, whilst a much greater augmentation is effected by the introduction of the aromatic radicles, the highest rotation being obtained in the case of the β-naphthylamide.

The two amides—tartranil and tartaric *p*-toluil—have much lower rotations than the corresponding diamides—tartranilide and tartaric *p*-toluidide—notwithstanding the cyclic groupings present in the former compounds. Similarly, low rotations have, however, also been found by Walden for malanil and malic β-naphthimide.

The molecular rotation of tartaric hydrazide is very slightly greater than that of tartramide, whilst that of the phenylhydrazide is much less than that of either; but, on the other hand, the hydrazones have very high rotations, a circumstance which is very probably due to the double linking which they contain, this grouping, whether between two atoms of carbon or between carbon and nitrogen, being known to exert a powerful influence on the rotation.

146. "*The Influence of Cyclic Radicles on Optical Activity: Tartaric* ar- *and* ac-*Tetrahydro-β-naphthylamides, Furfurylamide, and Piperidide.*" By P. F. Frankland and E. Ormerod.

The authors describe the preparation and properties of the above compounds. As anticipated the *ar*-tetrahydro-β-naphthylamide has a molecular rotation, $[M]_D\ 20° + 840°$, of the same order as those of the ordinary aromatic amides of tartaric acid, whilst the rotation of the *ac*-tetrahydro-β-naphthylamide, $[M]_D\ 20° + 240°$, is very much lower, being of the same order as those of the fatty amides: methylamide, $[M]_D\ 20° + 278°$, and ethylamide, + 279°.

It has been shown by P. Frankland and F. W. Aston (*Trans.*, 1901, lxxix., 514) that the rotatory influence of the pyromucyl radicle is very similar to that of the benzoyl and toluyl groups, from which is to be inferred that the furfuran and benzene rings resemble each other in rotatory effect. It would be expected, therefore, that the furfurylamide should have a molecular rotation of the same order as that of the benzylamide; as a matter of fact, they were found to be practically identical, thus:—

	$[M]_{D\ 20°}$.
Tartaric dibenzylamide	+ 300°
,, difurfurylamide..	+300—307°

Tartaric dipiperidide was found to be practically inactive.

147. "*The Rotatory Power of Maldiamide, Maldi-n-propylamide and Maldibenzylamide.*" By J. McCrae.

Maldi-n-propylamide and *maldibenzylamide* were prepared by heating diethyl *l*-malate with *n*-propylamine and benzylamine respectively. The propylamide melts at 125·5° and the benzylamide at 155·5°.

The specific rotations are:—In acetic acid ($c = 4·7$ to 5), maldiamide, −45·2°; maldi-*n*-propylamide, −47°; maldibenzylamide, −20·2°; in pyridine, maldiamide ($c = 2$), −57·7°; maldi-*n*-propylamide, −41·9°; maldibenzylamide, −32·4°.

By comparing these results with those obtained by Guye and Babel, and by Walden for the corresponding anilide and toluidides, it is seen that the effect produced on the rotatory power by the introduction of benzyl groups into maldiamide is similar to that caused by introducing fatty

alkyl groups, but is different from that brought about by replacing hydrogen of the amino-groups by aryl radicles.

148. "*Further Experiments with Phosphorus Sesquisulphide.*" By E. G. Clayton.

In a previous communication (*Proc.*, 1902, 129), it was shown that commercial phosphorus sesquisulphide of good quality had been found to give no reaction with Mitscherlich's test. With the object of studying under what conditions, oxidation, or a similar change, is promoted, and whether, by keeping, this compound acquires the property of yielding a luminous vapour when distilled with dilute sulphuric acid, the author has exposed specimens,

Experiment.	Atmosphere in which the phosphorus sesquisulphide was exposed.	Capacity and nature of vessel.	Time of exposure, in months.	Quantities taken of phosphorus sesquisulphide and 10 per cent acid. Grms.	C.c.	Observation.
1.	Dry air.	Tightly corked wide-mouthed bottle, about 90 c.c. capacity.	6	10	50	Negative result. No phosphorescence at any stage of the experiment, or in any portion of the apparatus.
2.	Air mixed with acetic acid and water-vapour.	Bell-jar, 4 litres capacity.	6	20	100	Result as above.
3.	Somewhat damp air.	Loosely stoppered wide-mouthed bottle, 300 c.c. capacity.	6	20	100	When 35 c.c. had distilled, a faint luminosity appeared on cooling in the upper coils of the spiral condenser and in the flask.
4.	Air saturated with moisture (*a*).	Glass shade, 21 litres capacity.	6	5	32	Strong phosphorescence in flask, connecting tube, and coils of condenser. On cooling, a vertical stream of luminous vapour descended into the flask.
5.	Air saturated with water-vapour (*a*).	Bell-jar, 4 litres capacity.	1	10	50	Similar reaction, but less marked.
6.	Atmosphere mingled with ammonia, carbon dioxide, and water-vapour.	Bell-jar, 4 litres capacity.	6	20	100	Excessively faint phosphorescence in upper coils, none in flask.
7.	Air impregnated with hydrochloric acid.	Glass shade, 21 litres capacity.	6	20	100	After 30 c.c. had distilled, phosphorescence appeared in upper coils and connecting tube, none in flask.
8.	Air over sulphuric acid. (The acid became brown and diluted in the course of the experiment, the air being evidently moist).	Glass shade, 3·75 litres capacity.	6	20	100	Towards the end of the experiment, a feeble glow appeared, visible in the upper coils of the condenser only.
9.	Atmosphere impregnated with nitrogen oxides.	Glass shade, 21 litres capacity.	2	10	50	Before 5 c.c. had distilled over, a very strong phosphorescence appeared on cooling, and a vertical stream of light descended into the flask, the interior of which became luminous for several minutes.
10.	Air of average humidity.	Beaker, 300 c.c. capacity.	2¾	20	100	When 30 c.c. had distilled, a distinct but slight luminosity was visible in the upper coils and connecting tube, although not in the flask.
11.	Air of average humidity.	Glass shade, 21 litres capacity.	2¾	20	100	After 40 c.c. had passed over, traces of phosphorescence were noticed in tube and coils, but none in flask.

(*a*) In these cases, a garlic odour was perceptible when the glass vessels were removed.

which had previously given negative results, for various periods under different conditions, the products being then subjected to Mitscherlich's test.

Experiments 9, 10, and 11 were made at a later date than the rest, consequently with a sample of sesquisulphide which had already been kept in the laboratory for a longer period. The last two experiments were made with the view of investigating the influence, if any, of the size of the vessel, but the results were not markedly different.

The temperature of the laboratory, of course, fluctuated considerably, but similar variations were experienced by samples exposed for the same periods.

From the results of these experiments, in which the author was assisted by Mr. G. N. Bacon, it is evident that good commercial phosphorus sesquisulphide undergoes little change if preserved in air of average dryness in nearly filled, well-closed vessels, but that the progress of the oxidation is appreciable in a damp atmosphere or in imperfectly closed vessels; this action takes place particularly rapidly in air saturated with moisture, and perhaps to the greatest extent in the presence of acid vapours, especially such as nitrogen peroxide.

Comparative experiments were made with yellow phosphorus, from which a luminous vapour passed over almost as soon as distillation began. With phosphorus sesquisulphide, on the other hand, the phosphorescence in most cases was seen only after the pressure had been diminished by the removal of the lamp, and after a considerable proportion of the liquid had distilled over. The author's experiments confirm J. Mai and F. Schaffer's observation (*Ber.*, 1903, xxxvi., 870; also *Journ. Soc. Chem. Ind.*, 1903, xxii., 511) that the glow differs from that of yellow phosphorus.

NOTICES OF BOOKS

The Analytical Chemistry of Uranium. By Harry Brearley, Joint Author of "The Analysis of Steel Works Materials." London, New York, and Bombay: Longmans, Green, and Co. 1903.

We have here the first of a very valuable series of analytical works, for we hope it is the author's intention to follow it up by others of a similar character. The author has been wise in his selection of uranium for the first issue, for on account of the recently discovered new properties of this element, and its close association with the group of radio-active bodies, it will certainly be of value to the many chemists who are turning their attention to that metal and its ores.

The introductory note gives the history of uranium, the localities where it has been found, &c., followed by "Modes of Determining Uranium," and its separation from many associated elements. The book ends by a good working description of the analysis of uranium ores, pitchblende, and carnotite, and a description of the metal and its alloys.

The Apothecaries' Hall Manual. For Students Preparing for the Dispenser's Certificate. By Mabel Thompson. London: Whittaker and Co.

This manual has been prepared to meet the requirements of students preparing for the assistants' examination of the Society of Apothecaries of London, and as it has been compiled by one who has passed that examination and is now engaged in the practical application of the knowledge so gained, it will doubtless be found of value to those commencing that course of study. The matter is naturally very condensed, for in a small book of 250 pages are set forth "The General Principles of Chemistry," "Preparation and Properties of the Elements and their more Important Compounds," "Tests for Alkaloids and some Organic Substances," Notes on the British Pharmacopœia, &c. It is only fair to the author to mention that the book professes to be a "supplement rather than a substitute for the numerous special works on the subject mentioned."

As far as can be seen the subjects are treated in a careful and accurate manner, and the work will doubtless be useful as a handy book of reference by students engaged upon absorbing the knowledge necessary to obtain the dispenser's certificate. There is a table of contents, and a good index.

The Art of Photographic Dodging by an Artful Photographic Dodger. By Richard Penlake and William Tylar. Birmingham: W. Tylar.

The above booklet is well worth the modest three-pence for pure fun, and in addition to that it is full of valuable little technical dodges told by one who has been "through the mill." There will be found in it something to learn for every photographer from the professional down to the freshest amateur, excepting only those of the "press the button class."

The Purification of Sewage and Water. By W. J. Dibdin, F.I.C., F.C.S. Third Edition, Revised and Enlarged. London: The Sanitary Publishing Company, Ltd. New York: D. van Nostrand Company. 1903.

The third edition of this comprehensive and useful work has been considerably enlarged. It contains in its present form most interesting accounts of the results of many investigations, and it is frequently shown that the author's forecasts in the previous editions have been fully confirmed by actual experience. The book contains statistics and information relating to the experiments performed at Leeds and Manchester for the elucidation of the problems connected with the disposal of sewage by the most efficacious and economical means, and also deals with the treatment of samples of trade refuse, and the purification and filtration of potable and other waters. The treatment afforded to the various subjects is exhaustive, and as a work of reference the book will be found invaluable.

Die Grundzüge der Monistischen und Dualistischen Weltanschauung. ("The Outlines of the Monistic and Dualistic View of the Universe"). By Gustav Portig. Stuttgart: Max Kielmann. 1903.

This small book is the first part of the second volume of the author's "Das Weltgesetz des Kleinsten Kraftaufwandes in den Reichen der Natur," the first volume of which appeared about a year ago. The whole of the second volume is to be published shortly, but meanwhile, for no very apparent reason, the first section of it appears in this form. The methods of the first volume are continued in this extract, which examines the philosophical outlines of monism and dualism and their relations to modern scientific knowledge. When dealing with monism in relation to chemistry the author incidentally treats his readers to a short review of the "Naturphilosophie" of Ostwald, who in Portig's opinion has fallen into grievous fundamental errors owing to his lack of philosophic training, and his ignorance of the difficulty of systematic philosophic reasoning. Such statements as these speak for themselves and prepare the reader for many other wild criticisms of monistic theories.

Electro-metallurgie: Die Gewinnung der Metalle unter Vermittlung des Elektrischen Stromes. Zweite Abtheilung. ("Electro-metallurgy: The Preparation of Metals by means of the Electric Current. Part II.). By Dr. W. Borchers. Leipzig: S. Hirzel. 1903.

The second and last part of this text-book of electro-metallurgy contains the description of the application of electrical methods to the preparation of the heavy metals,

excluding copper, which appeared in the earlier volume, and also discusses, though only very shortly, the preparation of some metallic compounds, such as carbides and silicides. An index to the whole book is added. The facts that this is the third edition of the original, and that English, French, and Spanish translations have appeared show that the book has been appreciated, and it will no doubt continue to be regarded for some time as the standard work of its kind and size on the subject.

CORRESPONDENCE.

LATENT HEATS OF FUSION OF METALS.

To the Editor of the Chemical News.

Sir,—I have just been reading Mr. Crompton's paper on the subject occurring in your issue of November 13th (vol. lxxxviii., p. 237), there described as read before the British Association at the Southport meeting.

I desire to claim priority in stating the law there set forth. You will find it fully discussed in a letter from me published in the Chemical News for November 26th, 1897 (vol. lxxvi., p.) 264. From that letter I may quote the following expression of the law of liquefaction heat:—

"The molecular liquefaction heat of a monatomic liquid is equal to the total kinetic energy of a monatomic gas molecule at the same temperature.

"This for each grm.-molecule can be easily calculated, as is well known. Taking t as the absolute temperature it is equal to about 3 t calories."

It will be observed that I here used the value 3 (as given by Ostwald, "Allgemeine Chem.," vol. ii., Chap. iv.), whereas Mr. Crompton uses the value 2·96 t. Otherwise the two statements are identical, though the illustrative table is not drawn up in quite the same form.

The law above stated does not for some reason seem to have attracted very much notice at the time, but I think it is of very considerable importance, throwing great light as it does upon the mechanism of liquefaction, and also upon the molecular condition of liquids. It seems to show that the polymerisation of molecules in the liquid state is considerably smaller than is commonly assumed. With your permission I shall be pleased to say a few words further on this shortly.—I am, &c.,

P. J. Beveridge, M.A., B.Sc.

7, Bridge Place, Chester,
November 21, 1903.

P.S.—May I, at this late date, correct an oversight in the statement for the two non-metallic elements referred to in the earlier letter. Br and I should read Br_2 and I_2.

ASSOCIATION OF THE ELEMENTS.

To the Editor of the Chemical News.

Sir,—It is a well known and remarkable fact that certain elements invariably accompany others when found in nature. Thus, Ag seems always to be present to a greater or less extent in Pb. Cd is almost invariably found in Zn. S usually contains minute traces of Se.

And this association occurs in spite of the fact that these elements are often possessed of very different atomic weights and densities, and so would not be expected to be deposited together in primordial times by a simultaneous condensation from a glowing gaseous earth.

In view of the recent observation that helium gas is so often found associated together with certain heavy minerals, and seems to be produced from radium contained therein by some mysterious process of atomic decomposition, may not we reasonably enquire whether in other cases where certain elements occur constantly associated together the association is due to a similar cause, viz., the very slow production of one element from the other by some slow process of atomic decomposition?

So that in the course of ages, perceptible amounts of Ag may be produced from Pb, and of Se from S, and so on.

The fact that every physical property discovered in one element has always been found to be shared to a greater or less extent by every other, suggests that radium would not be the only element which can, by a process of atomic decomposition, give rise to others.

The mere possibility of such a transformation assumes tremendous importance from its bearing on geology and on the distribution of minerals throughout the earth.

A very slow continuous effect acting for many ages can produce results of the very greatest magnitude.—I am, &c.,

Geoffrey Martin.

Kiel, November 17, 1903.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 18, November 2, 1903.

A New Variety of Filiform Carbon.—M. Constant and Henri Pélabon.—The carbonisation of fatty oils for the preparation of metallurgical coke leads to the formation of certain deposits having a filiform appearance. These deposits are formed in the portion of the furnace exposed to a very high temperature, and above the coke layer—in fact, where the action of radiation is most direct. The authors examines a single thread, and find the mean length to be 0·05 metre, but some are 0·08 metre long. At about 585°, when heated in a current of pure dry oxygen, the thread begins to form carbon dioxide.

Separation and Estimation of Iron and Phosphoric Acid from Water.—H. Causse.—In order to precipitate the iron and the phosphoric acid in potable waters, the author uses chloro-mercuriate of *p*-amidobenzene-sulphonate of sodium. The mercury bichloride is here the active agent, oxidising the ferrous and phosphoric combinations. It precipitates the iron in the form of sesquioxide, the phosphoric acid in the form of insoluble mercury phosphate if the water is impure; whilst under the condition where the quantity of iron is at a minimum, protochloride of mercury is also obtained. The author thus compares the waters of the Rhone, Saône, and spring water from calcareous earth.

A Method of Synthesis of Symmetric Dihalogen Derivatives of Benzophenone.—F. Bodroux.—Carbonic anhydride reacts on bromides of parachlorophenyl magnesium and of parabromophenyl magnesium, giving at the same time a monosubstituted benzoic acid and a dihalogen symmetric derivative of benzophenone. When the reaction takes place at the temperature of boiling ether, the latter substance predominates. If, on the contrary, the reaction takes place at a low temperature, the substituted benzoic acid forms the larger portion.

Application of Pyridine to the Preparation of certain Amido-derivatives.—P. Freundler.—The author employs pyridine for the preparation of various secondary and tertiary aromatic amides, such as benzenesulphanilide, dibenzenesulphanilide, *p*-toluylbenzanilide, benzoyl-benzenesulphanilide, &c. This latter substance has never been obtained by heating benzoyl chloride with benzene sulphanilide. The author also utilises the properties of pyridine to solve the question of the isomerism of dibenzanilide in a definite manner. The preparation of the mixed amides of the fatty and aromatic radicles by means of pyridine is effected in a less regular manner. He

establishes the fact that the chloride of the aromatic acids very easily displaces the fatty radicles, even when not used in excess.

Use of Magnesium Amalgam in Organic Chemistry.—Louis Meunier.—Magnesium amalgam and the alcoholates resulting from its use can be employed in a number of syntheses, and especially in the preparation of diphenylmethane and the ethyl derivatives of ethyl malonate. The author proves that the action of the mixed organo-magnesium salts described by Grignard on ethyl malonate acts first on the group $CH_2<$, then on the ether-salt functions, whilst the action of magnesium in the state of amalgam on the same compound only attacks the group $CH_2<$.

Orthotoluic Aldehyde.—H. Fournier.—The author obtains pure orthotoluic aldehyde by the oxidation of the corresponding alcohol. He also finds that the use of semicarbazide to identify the aromatic aldehydes presents certain difficulties, chiefly due to its high price and the very slight differences existing between the fusion-points of the semicarbazones. It can, however, be advantageously replaced by asymmetric benzyl phenylhydrazine, which acts immediately in the cold on aldehydes, giving bodies which are very easily purified. One or two crystallisations from alcohol produces these in the form of white silky crystals, unchangeable in light and air. In this way the benzylphenylhydrazones of orthotoluic aldehyde, paratoluic aldehyde, phenylacetic aldehyde, and *p*-ethylbenzoic aldehyde were prepared and identified.

— —

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxix., No. 9.

Solubility of Hydrated Sulphate of Calcium in Solutions of Sea-salt.—Alex d'Anselme.—Will be inserted in full.

Synthesis of a New Aromatic Hydrocarbide Decacyclene (Trinaphthylenebenzene), and of a Derivative of Thiophene having a Red Colour, Dinaphthylenethiophene. — C. Dziewonski. — Already noticed.

Some Experiments on the Constant Molecular Elevation of the Boiling-point of Nitrobenzene.—Paul Bachmann and Charles Dziewonski.—The authors give their results in the form of tables, and, as a final figure, they find 51·03 for nitrobenzene at 89·85 calories.

The Nitration of Furfurane. Acetine of Nitrosuccinic Aldehyde. Fumaric Aldehyde and its Derivatives.—R. Marquis.—Already noticed.

New Synthesis of Orthodiazine.—R. Marquis.—Already noticed.

Action of Pentachloride of Phosphorus on Isopyromucic Acid.—G. Chavanne.—Small quantities of perchloride of phosphorus (20 grms.) are thrown gradually into a chloroformic solution of pure isopyromucic acid (45 grms.) quite free from pyromucic acid. This brings about a rise of temperature and a considerable evolution of nitric acid. After evaporating off the chloroform, a brown crystalline mass is obtained, which is crushed on a porous porcelain plate and re-crystallised in chloroform or boiling anhydrous acetic ether. On cooling, these solvents give very refrangible prisms fusing at 138°, insoluble in water, ether, and cold alcohol, and soluble in chloroform, benzene, acetic acid, and anhydrous acetic ether. The evaporation of the benzenic solution gives beautiful crystals.

Acetylised Derivatives of Isopyromucic Acid: Acetate, Benzoate, Pyromucate of Isopyromucyl.—G. Chavanne.—Already noticed.

Bromo-isopyromucic Acid.—G. Chavanne.—Already noticed.

New Method for the Preparation of $\alpha\alpha'$-Diphenylpyridine Carbonic Acid.—T. Klobb.—Eight grms. of diphenacylcyanacetate of methyl or of ethyl, 20 grms. of pure hydrate of potassium, and 500 grms. of alcohol at 95° are boiled in a flask with a vertical condenser. To prevent as much as possible the formation of the blue substance formed by oxidation, the water-bath must be already heated up to 100°; to the boiling alcohol we add successively the potash and the diphenacylcyanacetic ether, and keep the whole boiling briskly, so as to prevent the entry of air. The liquid, which is at first a violet-brown, gradually loses its colour, and generally after four hours' heating, but sometimes less, takes a madder colour—a sign of the end of the operation. The cold mixture is left for twenty-four hours; this facilitates the decoloration. The ammoniacal alcohol is driven off by distillation, taken up with 500 grms. of water, and allowed to stand for another day or two; an impure resinous substance separates out. The alkaline liquid, which is now barely coloured, is filtered; acidulate with sulphuric acid, and the new acid is precipitated in white flocculent particles, which are washed and dried at 100°. It can be purified with alcohol, but nitrobenzene is preferable. After two crystallisations in this solvent we obtain a compact mass of white needles, which must be washed with cold alcohol.

The Mixed Ureas of Piperidine and of the Aromatic Amines.—M. Bouchetal de la Roche.—By reacting with piperidine on the ureas, the author has prepared various mixed ureas of piperidine and the corresponding amines, getting a return of 90 per cent. One molecule of urea was heated for two hours at 170°, in a sealed tube with an excess of piperidine (three or four molecules). The contents of the tube were taken up with a little alcohol at 95°, the solution is neutralised with dilute hydrochloric acid, and a large excess of water added. The urea is deposited in small crystals. Filter, wash with water, and re-crystallise in alcohol. These ureas are much more soluble in the organic solvents than the corresponding symmetric ureas.

Detection of Saccharine in Wines, Beers, &c.—C. Boucher and F. de Boungne.—The beer is submitted to the direct action of a solution of permanganate of potassium at 1/100th in the presence of a few drops of sulphuric acid. It is better to operate in the cold when only traces of saccharine are suspected. The excess of the reagent is removed by means of sulphurous acid, and there remains only to extract the saccharine by ether alone. With wine it is best to operate at the temperature of the water-bath.

MISCELLANEOUS.

Chemical Society Research Fund.—A meeting of the Research Fund Committee will be held in December. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before December 7th.

Illustrated Scientific News.—We are pleased to be able to announce the recent completion of the first volume of this interesting and valuable paper. It has fully carried out the promise made on the occasion of its first appearance. A strong feature of this publication is its accuracy and the entire absence of exaggeration too often met with in those papers in which science is put before the reader in a so-called popular form. The editor is to be congratulated on the success of his efforts, which have produced a paper completely up to date and thoroughly trustworthy. As an example of the versatile character of the contents of this paper we may mention that recent numbers contain articles on "The Limits of Microscopic Vision," "The Eiffel Tower, its Uses and Prospects," "Comets and their Tails," "The Radium Theories," "Earthquakes and Earth Tremors," "The British Association, 1903," and many others, the more important ones being illustrated. The paper also contains a monthly letter of Continental physical news, reviews of books, recent patents, and astronomical notes for the month, and other interesting features.

Fractional Combustion of a Mixture of Methane and Hydrogen by Winkler's Method. — K. V. Charitchkof. — Experiments have been carried out on various mixtures of hydrogen and methane. It was found that at 90° the combustion of the hydrogen was complete, but there is always a certain quantity of CO_2 formed; the combustion of the methane mixed with hydrogen may be noticeable at this low temperature. In principle, the method is not applicable to the separation of H and CH_4, even when there is only a small quantity of H; in this latter case, however, it may be used, but it is necessary to measure the volume of CO_2 formed. It must be observed that with time the palladium-coated asbestos loses its catalytic properties. The best method of absorbing the hydrogen in the mixture is to use palladium sponge, as Hempel advised, but it is unnecessary to heat to 120°, a temperature of 70° is quite sufficient.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiv., p. 710.

Preparation of Zirconia.—E. Wedekind.—The method adopted by the author is as follows:—An intimate mixture of 20 parts of zircon, 12 parts of lime, and 7 parts of carbon is heated in a carbon crucible in the electric furnace. The crucibles, which are only three-quarters full and uncovered, are heated by means of a current of 1000 ampères and 50 volts for seven minutes. After the reaction the graphite cover is put on to prevent oxidation. After cooling, wash with cold water, then with hydrochloric acid. The carbide is then dissolved in aqua regia; filter through asbestos, and evaporate to dryness. The iron is removed from the residue, either by precipitating the ZrO_2 and FeS by means of sulphide of ammonium, and then dissolving the sulphide of iron with sulphurous acid, or by precipitating the sulphide of iron with sulphide of ammonium in the presence of tartaric acid. When treated with a current of chlorine, carbide of zirconium gives the anhydrous chloride, $ZrCl_4$, which dissolves in water, forming the oxychloride. This oxychloride can be obtained in a well crystallised form by dissolving the chloride in hydrochloric acid. When heated to 100—110° it becomes less soluble in water.—*Zeit. Anorg. Chem.*, vol. xxxiii., p. 81.

Anodic Decomposition of Solutions of Cobalt and of Nickel.—Alfred Cohen and Moritz Gloser.—A. Cohen has shown the difference of susceptibility with which nickel and cobalt appear to form higher oxides (*Zeit. Phys. Chem.*, vol. xxv., p. 651). In collaboration with M. Gloser, he has examined the anodic decomposition of solutions of nickel and cobalt. In slightly alkaline solutions, the sulphates of these metals give oxides at voltages of 1·20 for cobalt and 1·30 for nickel. In slightly acid solutions nickel does not form an oxide, and cobalt requires 1·52 volts. In strongly acid solutions no oxide is formed either of nickel or cobalt. Precipitated oxide of cobalt dried at 40° has a composition which varies from $Co_2O_3.3H_2O$ and $Co_2O_3+2H_2O$. Cobalt and nickel can be separated electrolytically. The conductivity of the solutions must be increased by the addition of sulphate of potassium. A platinum cathode is used, and bichromate of potassium as a depolarising agent. The electrolysis is carried out in hot solution with a current of 2·3 to 2·4 volts, and 0·10 to 0·15 ampère, and the separation is complete. This method is very useful for the detection of cobalt in the presence of nickel; cobalt, even in small quantities, gives a dark deposit on the platinum anode in neutral solution. —*Zeit. Anorg. Ch.*, vol. xxxiii., p. 9.

MEETINGS FOR THE WEEK.

MONDAY, 7th.—Society of Arts, 8. (Cantor Lectures). "The Mining of Non-Metallic Minerals," by Bennett H. Brough.
— — Society of Chemical Industry, 8. "Cyanide Manufacture," by Dr. J. Grossmann.
TUESDAY, 8th.—Faraday Society, 8. "Total and Free Energy of the Accumulator" (adjourned Discussion), by R. A. Lehfeldt, D.Sc. "Bitumen in Insulating Compositions" (Part I.), by D. A. Sutherland, F.I.C., F.C.S. "Notes on Aluminium Welding," by Sherard Cowper-Coles. "Electro-chemical Installation at the Borough Polytechnic Institute," by F. M. Perkin, Ph.D.
WEDNESDAY, 9th.—Society of Arts, 8. "Furnaces Suitable for Jewellers' Work, Enamelling, Art Casting, and other similar Industries," by Henry Hardinge Cunynghame, C.B.
THURSDAY, 10th.—Society of Arts, 4.30. "India's Place in an Imperial Federation," by J. M. Maclean.
FRIDAY, 11th.—Physical, 8. (At the Royal College of Science, South Kensington). "A Method of Mechanically Reinforcing Sounds," by Rev. T. C. Porter. "The Simmance-Abady 'Flicker' Photometer," by Messrs. Simmance and Abady. Exhibition of a Conductometer, by R. Appleyard. A Model to Illustrate various Properties of Wave-motion, by Prof. L. R. Wilberforce.

TO CORRESPONDENTS.

S C W.—The thing is impossible without destroying the oil.

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Vol. LXXXVIII., No. 2298.

THE SLOW COMBUSTION OF METHANE AND ETHANE.*

By WILLIAM A. BONE.

I MAY perhaps be allowed to explain my reasons for reopening what I am well aware is one of the most controverted questions in the whole domain of chemistry. Let me say at once that I have no new general theory of hydrocarbon combustion to bring forward; but during the past three or four years I have, in conjunction with two of the research students at Owens College (Messrs. R. V. Wheeler and W. E. Stockings), been engaged upon an investigation on the slow combustion of methane and ethane at temperatures below their ignition-points, the results of which throw some new light on the question at issue. It is my intention to extend the work to other typical hydrocarbons in the hope that the gradual accumulation of experimental facts may at some future time provide a sure basis for a general theory of hydrocarbon combustion. Meanwhile it seemed to me that the meetings of this Chemical Section afforded a fitting opportunity of communicating and discussing these new observations, of obtaining suggestions for future work, and possibly, also, of arranging some form of co-operation among those workers who are specially interested in this field of inquiry.

It seems to me unnecessary to make more than a passing reference to the theories which up to the present have been advanced to explain the mechanism of hydrocarbon combustion. I must, however, say a word with regard to two of them which involve the idea of the "*preferential*" combustion, either of hydrogen or of carbon. The older idea, that in a defective oxygen supply the hydrogen of a hydrocarbon burns preferentially to the carbon, is unsupported by experimental evidence, and I suppose now hardly finds acceptance among chemists at any rate. On the other hand, the opposite view, that the carbon burns preferentially to the hydrogen, was put forward, originally by Kersten in 1861 I believe, to explain the well-known fact that when such a hydrocarbon as ethylene is exploded with just sufficient oxygen to burn the carbon to carbon monoxide, the cooled products consist of carbon monoxide and free hydrogen—

$$C_2H_4 + O_2 = 2CO + 2H_2.$$

Professor Smithells in 1892 was led to indorse this view as the result of his analyses of the interconal gases of hydrocarbon flames.

It seems to me that the idea of "*preferential combustion*," whether of hydrogen or of carbon, is closely allied to the old doctrine of "*elective affinity*," and that it is hardly to be reconciled with modern conceptions of the nature and conditions of chemical change in a homogeneous system. Furthermore, it may be pointed out that the evidence usually adduced in support of the contention that carbon burns preferentially to hydrogen is wholly derived from experiments on the oxidation of hydrocarbons at very high temperatures, either in the flame, or in the explosion wave. Under these conditions it is practically impossible, by any means at our command at present, to distinguish the character of the *primary* oxidation in the case of a hydrocarbon, for since the velocities of all the reactions concerned are enormously great, the final state of equilibrium is almost instantaneously established.

The experiments on the slow combustion of methane and ethane, which have led me to make this communication, have been carried out at temperatures far below the ignition-points of the gases—that is to say, at temperatures where the oxidation velocities are sufficiently small to allow of their being easily measured. It is also important to observe that either of the hydrocarbons in question interacts with oxygen at temperatures below those at which the velocities of any of the undermentioned possible secondary changes become appreciable :—

i. $2H_2 + O_2 = 2H_2O$.
ii. $2CO + O_2 = 2CO_2$. (moist)
iii. $CO + H_2O \rightleftarrows CO_2 + H_2$.
iv. Reduction of CO_2, or of H_2O, by carbon.

Therefore, by suitably choosing our temperature conditions we have been able to exclude the possibility of these reactions occurring, and so to prevent the complete masking of the *primary* reaction by secondary changes.

The details of these experiments either have been, or shortly will be, published elsewhere (*Trans. Chem. Soc.*, 1902, lxxxi., 535; 1903, lxxxiii.), and we need therefore only here indicate the general character of the results.

In the first place, we should say that the mixtures of methane (or ethane) and oxygen employed usually contained just sufficient oxygen to burn the carbon of the hydrocarbon to carbon monoxide (*e.g.*, mixtures of two volumes methane with one volume oxygen, or of equal volumes of ethane and oxygen).

The lowest temperature at which such mixtures of methane and oxygen interact, when sealed up in a borosilicate glass bulb at atmospheric pressure, and afterwards placed in a constant temperature air-bath, is somewhere about 300°; in the case of the mixtures of ethane and oxygen it is about 225°. At all temperatures ethane is oxidised much more rapidly than is methane, other conditions being equal.

Under such conditions a portion of the hydrocarbon is burnt to, finally, carbon dioxide, carbon monoxide, and steam, *without any liberation of free hydrogen or separation of carbon*, while a portion of the original hydrocarbon always remains intact.

Below are tabulated the analyses of the products from two typical experiments :—

Products from Mixture $CH_4 = 66{\cdot}9$, $O_2 = 33{\cdot}1$, *maintained Seven Days at* 350°.		*Products from Mixture* $C_2H_6 = 49{\cdot}8$, $O_2 = 50{\cdot}2$, *maintained Fifteen Hours at* 250°.	
CO_2	14·0	CO_2	15·9
CO	16·3	CO	41·2
O_2	0·9	O_2	nil
CH_4	68·8	C_2H_6	42·9
Per cent contraction in volume on opening cooled bulb under mercury (nearly)	32·0		34·76

We next devised an apparatus in which the reacting gaseous mixtures can be continuously circulated day and night, at a practically uniform rate, (1) over a surface maintained at a constant temperature; and (2) through suitable washing and cooling arrangements for the removal of soluble or condensable intermediate products. A manometric arrangement enables us to take pressure records of the gas in the apparatus at regular time-intervals throughout a given experiment, which may often extend over many consecutive days and nights. The records so obtained show, in the case of both methane and ethane, a regular and continuous fall of pressure throughout the oxidation.

The experiments with methane reveal the fact that formaldehyde plays an important *rôle* as an intermediate

* A Paper read before the British Association (Section B), Southport Meeting, 1903.

product; that, indeed, the oxidation involves at least two distinct stages, namely:—

1. A primary oxidation to formaldehyde and steam—

$$H\cdot\dot{C}(H)\cdot H + O:O = H\cdot\dot{C}(H):O + H_2O.$$

2. The subsequent further rapid oxidation of the formaldehyde to carbon monoxide, carbon dioxide, and steam. This may best be considered as the result of two simultaneous reactions, namely:—

$$(a)\quad H\cdot\dot{C}(H):O + O:O = O:C:O + H_2O,$$

$$(b)\quad H\cdot\dot{C}(H):O + O:O + H\cdot\dot{C}(H):O = 2CO + 2H_2O,$$

possibly the latter may involve the formation and very rapid decomposition of formic acid. Thus—

$$O:\dot{C}(H)\cdot H + O:O + H\cdot\dot{C}(H):O = 2\left[O:\dot{C}(H)\cdot OH\right] = 2CO = 2H_2O.$$

In the case of ethane we are able to distinguish the successive formations of (1) acetaldehyde, and (2) formaldehyde, as intermediate products. The experimental results are consistent with the following view of the case, namely:—

1. That the primary oxidation involves the formation of acetaldehyde and steam—

$$CH_3\cdot CH_3 + O_2 = CH_3\cdot CHO + H_2O.$$

2. That the acetaldehyde is further rapidly oxidised to carbon monoxide steam and formaldehyde—

$$H\cdot\dot{C}(H)\cdot H + \begin{matrix}O\\\ddot{O}\end{matrix} = H\cdot\dot{C}(H):O.$$
$$\qquad\qquad\qquad\qquad\qquad\quad CO\ H_2O$$

3. That the formaldehyde suffers further oxidation as indicated above.

These views, it may be stated, are supported by experiments on the oxidation of acetaldehyde.

I wish it to be understood that I have provisionally adopted the explanations just given of the oxidation stages of methane and ethane as a convenient working hypothesis because they express most simply the observed facts. Professor Armstrong has recently given us (*Trans. Chem. Soc.*, lxxxiii., 1088) a very suggestive general theory of combustion which embodies his dictum that chemical interchange and electrolysis must be regarded as interchangeable equivalent terms. Applied to hydrocarbons (*e.g.*, methane) the theory involves the successive "hydroxylation" of each hydrogen by an indirect process, the oxygen being transferred electrolytically across "conducting" water, as indicated by the following scheme:—

1. $CH_4 + OH_2 + O_2 = CH_3(OH) + H_2O_2$
2. $CH_3OH + OH_2 + O_2 = CH_2(OH)_2 + H_2O_2$.
3. $CH_2(OH)_2 + OH_2 + O_2 = CH(OH)_3 + H_2O_2$
4. $CH(OH)_3 + OH_2 + O_2 = C(OH)_4 + H_2O_2$.

The hydrogen peroxide formed being in part decomposed by heat, and in part acting as depolariser.

The hydroxylated molecules thus produced may decompose, as for instance:—

5. $CH_2(OH)_2 = CH_2O + H_2O$.
formaldehyde.

and then the formaldehyde is further indirectly oxidised to (1) formic acid, (2) carbonic acid, thus:—

6. $O:C:H_2 + OH_2 + O_2 = \begin{matrix}HO\\H\end{matrix}\!>\!C:O + H_2O_2$.

7. $\begin{matrix}HO\\H\end{matrix}\!>\!C:O + OH_2 + O_2 = \begin{matrix}HO\\HO\end{matrix}\!>\!C:O + H_2O_2$.

The formic and carbonic acids thus produced then decompose as follows:—

8. $\begin{matrix}HO\\H\end{matrix}\!>\!C:O = CO + H_2O$.

9. $\begin{matrix}HO\\HO\end{matrix}\!>\!C:O = CO_2 + H_2O_2$.

It does not come within the province of this paper to discuss this electrolytic theory of chemical change; it should, however, be pointed out that Professor Armstrong's views demand the formation of an alcohol in the *primary* oxidation of a saturated hydrocarbon. Although I have never failed to obtain a marked formation of aldehydes in my experiments on methane and ethane, I have so far searched in vain for alcohols; if the latter are produced during the primary oxidation, they are very rapidly further oxidised to the corresponding aldehydes which must be presumed to be more stable under these conditions.

The question now arises whether these reactions which undoubtedly occur at low temperatures also occur at the higher temperatures of hydrocarbon flames. My own view is this:—The velocities of these "low temperature" reactions will rapidly increase as the temperature rises, and so long as aldehydes can exist, aldehyde formation will occur. But aldehydes themselves decompose at high temperatures; thus acetaldehyde is known to yield carbon monoxide and methane—

$$CH_3\cdot CHO = CH_4 + CO,$$

and similarly formaldehyde yields carbon monoxide and hydrogen—

$$H\cdot CHO = CO + H_2,$$

and possibly within certain temperature limits these reactions are reversible.

The production of formaldehyde in the oxidation of methane, for example, will only be limited by the temperature at which formaldehyde is incapable of existence, whatever that may be.

We shall have to take into account similar considerations in discussing other probable changes, as, for example, (1) the further oxidation of aldehydes, and (2) the purely thermal decomposition of hydrocarbons. All these possible reactions call for further careful investigation. As yet we have so few well-established data that it seems premature to formulate general theories. The subject is very complex, and is beset with many and great experimental difficulties, but it is surely within our power to overcome them, especially if a sufficient number of workers will co-operate.

Dr. T. L. Phipson's recent work, "Researches on the Past and Present History of the Earth's Atmosphere," has just been translated into Japanese by Prof. Sakatibara, Lecturer on Pharmacy at the Kato Hospital, Tokio.

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ON ACRIDINES.*

By ALFRED SENIER, Ph.D.,
Professor of Chemistry in Queen's College, Galway.

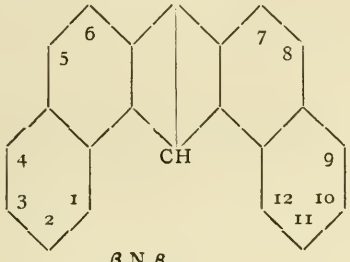
(Continued from p. 269).

V. *Naphthacridines.*

The naphthacridines are obtained by methods analogous, generally, to those for the preparation of acridines. They are stable crystalline compounds with the physiological action and the characteristic fluorescence of their simpler analogues. Like the latter, they form dihydrides, salts, alkhalides, and, as Mr. Goodwin and I find, they also form dihalides.

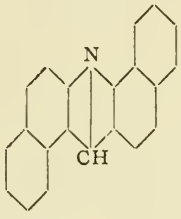
1. *Possible Isomeric Types :—*

A.



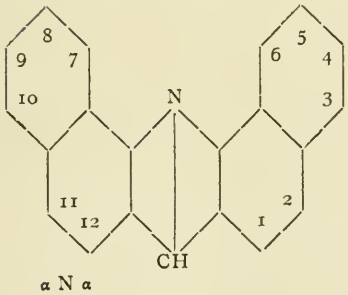
β N β
α C α (Reed).

B.



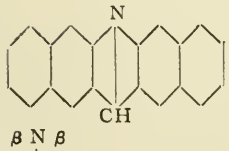
β N α
α C β (Ullmann).

C.



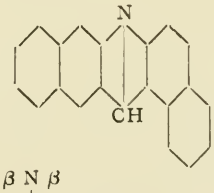
α N α
β C β (Senier and Goodwin).

D.



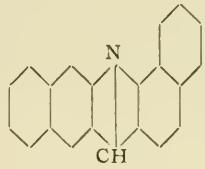
β N β
β C β (Unknown).

E.



β N β
β C α (Strohbach).

F.

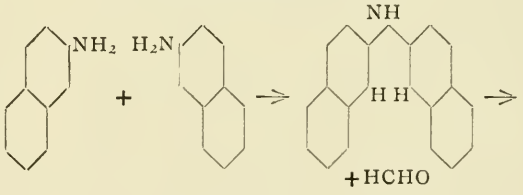


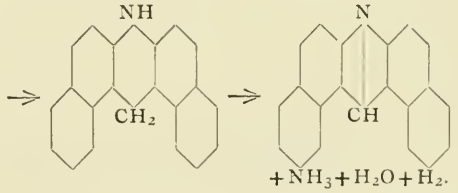
β N α
β C β (Unknown).

The notation is, I think, more convenient than that used by Ullmann (*Ber.*, 1903, xxxvi., 1037) after Graebe, or by Möhlau and Haase after Strohbach (*Ber.*, 1901, xxxiv., 4147). The numbering is taken from Möhlau and Haase (*Ber.*, 1902, xxxv., 4173).

2. *Formation and Constitution :—*

i. *Diamine and Aldehyde Method.*—The first naphthacridine, *ms*-phenylnaphthacridine, was obtained by Claus and Richter (*Ber.*, 1884, xvii., 1590) by condensing benzoyldi-β-naphthylamine by means of a dehydrating agent. This may be regarded as a modified aldehyde diamine method. The first simple naphthacridine was prepared by Reed (*Journ. Prakt. Chem.*, 1886, [2], xxxiv., 160; 1887, xxxv., 298), who condensed two molecules of β-naphthylamine with formaldehyde (methylal and hydrochloric acid). That this naphthacridine is β N β / α C α has been generally accepted after the evidence adduced by Strohbach (*Ber.*, 1901, xxxiv., 4148) as to the greater readiness with which the α-position substitutes. Di-β-naphthylamine and naphthacridine dihydride are formed doubtless as intermediate products, thus :—



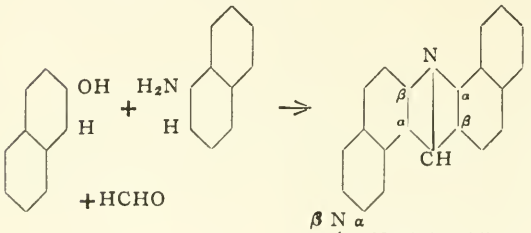


β N β
α C α Naphthacridine (Reed).

This reaction is the subject of two important papers by Morgan (*Journ. Chem. Soc.*, 1898, lxxiii., 536; 1900, lxxvii., 814), who describes another very curious compound obtained in the same reaction, "isonaphthacridine." Möhlau and Haase (*Ber.*, 1902, xxxv., 4164) in a recent paper have re-investigated this compound, and its constitution is still a problem of great interest. Modifications of Reed's method have been employed by Möhlau and Haase (*Ber.*, 1902, xxxv., 4172; 1903, xxxvi., 591), and recently Ullmann and Fetvadjan (*Ber.*, 1903, xxxvi., 1027) from β-naphthol, α-naphthylamine, and

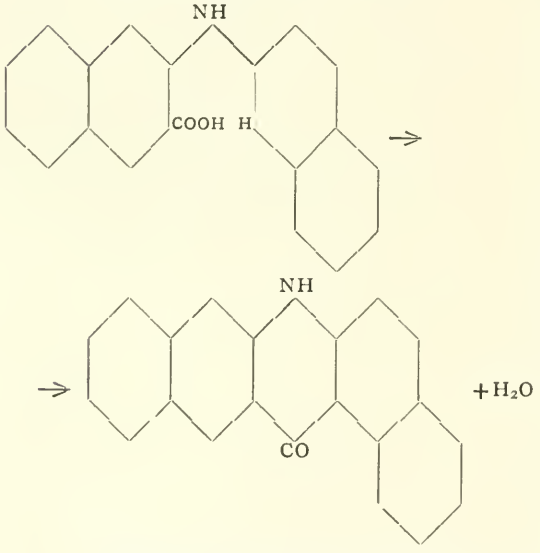
* Abstract of a Paper read before the British Association (Section B), Southport Meeting, 1903.

formaldehyde, have discovered a new naphthacridine, the β N α / α C β isomeride (Formula B.), thus :—

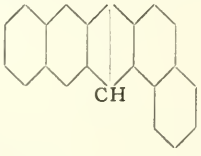


β N α / α C β Naphthacridine (Ullmann and Fetvadjan).

ii. *Diamine and Acid Method.*—Ris (*Ber.*, 1883, xvii., 2029), in applying this method to naphthacridines, prepared the phenylnaphthacridine of Claus and Richter from di-β-naphthylamine and benzoic acid. Möhlau obtained the acridone of a new type from di-β-naphthylamine-2 : 3-monocarboxylic acid, thus :—

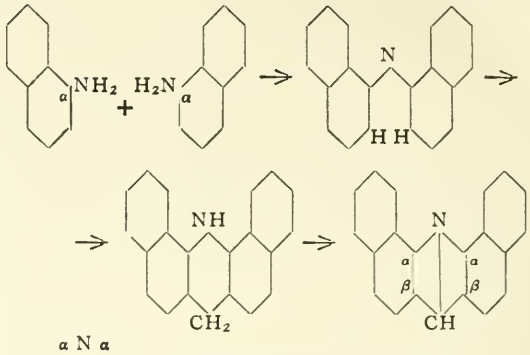


Strohbach by reducing this acridone prepared the corresponding acridine (Formula E.) :—



β N β / β C α Naphthacridine (Strohbach).

iii. *Methylene Di-iodide and Diamine Method.*—By this method Mr. Goodwin and I (*Journ. Chem. Soc.*, 1902, lxxxi., 280) obtained Reed's naphthacridine working with β-naphthylamine, while in the corresponding experiment with α-naphthylamine we succeeded in isolating a new type α N 1 / β C β naphthacridine, thus :—



α N α / β C β Naphthacridine (Senier and Goodwin).

Two nitro-derivatives of this base were obtained and a disulphonic acid recently described by Möhlau and Haase (*Ber.*, 1902, xxxv., 4173) belongs to the same type.

I have just succeeded in obtaining the β N α / α C β base of Ullmann and Fetvadjan by the methylene di-iodide method.

(To be continued).

ESTIMATION OF MORPHINE IN OPIUM.

By P. L. ASLANOGLOU.

This no doubt will add one more process for the estimation of morphine in opium to the many already existing, but it must not be assumed that the past researches of my *confrères* have been disregarded by me; on the contrary, having worked with their methods I failed to obtain satisfactory results, perhaps owing to their not being clearly explained. I have, however, tried to the best of my knowledge, after having experimented a great deal, to work out an easy and quick method for the estimation of morphine in opium.

Take 10 grms. or so of a fair sample of opium which has been taken from the bulk and well mixed in a machine, and rub it down well in a small glass mortar with a small quantity of distilled water, and when this has extracted what it can from the opium put it into a beaker, and again add water to the mortar, rubbing it down until all the 10 grms. of opium has been well mixed with water, using only 150 c.c. of water for that manipulation. This should be left to stand for twelve hours in soak, and then decant the brownish red liquid on to a filter, using double filters, leaving the opium behind. Add to it another 150 c.c. of water, and let it stand in soak for an hour or so, stirring from time to time. The first filtrate containing the alkaloids of opium is evaporated to dryness on a water-bath. The second portion of the 150 c.c. aqueous extract of opium is filtered as before, and the filtrate evaporated to dryness in the same evaporating basin which has been used for the first evaporation; the remaining opium is for a third time treated with 200 c.c. of water filtered as before, and evaporated. This dry aqueous extract represents the 10 grms. of opium taken. It is then dissolved in 75 c.c. of water, and filtered, using double filters; the basin and filter-paper are well washed with 25 c.c. more of water till the whole measures 100 c.c. To this 100 c.c. filtrate containing the alkaloids of the opium, 25—30 c.c. of 94 per cent alcohol are added, and well stirred for half-an-hour. After this 3—4 c.c. of 10 per cent solution of ammonia (sp. gr. 0·959) are added, and well stirred for half-an-hour,

and left for twelve hours to precipitate; it is best not to leave it more than twelve hours.

3·5—4 c.c. of 10 per cent solution of ammonia is to be added for 10 grms. opium for analysis containing 9—11 per cent morphine, but if the opium contains between 11—13 per cent morphine the ammonia ought to be increased to between 4—5 c.c.; however, experience will show this to the analyst. In fact the correct way will be to take a very small portion of the filtered aqueous extract, dilute it with water, and titrate it with N/10 NH_3, using as indicator phenolphthalein. Once we know the percentage of acidity of the solution, we can estimate accordingly the amount of NH_3 required for the whole solution in order to precipitate the morphine.

After the twelve hours have elapsed, pour the liquid through a tared filter-paper, leaving the precipitated morphine behind in the flask (flasks should be used with good indiarubber corks or glass-stoppers for precipitating the morphine, and not open beakers). Then 25 c.c. of water is added to it to wash it, and the washings with the morphine are transferred to the tared filter-paper, and washed well with another 25 c.c. of water; let it drain well, and partly dry in the oven at 60° C. When this is done, the filter with the morphine is well washed with pure ether; let it drain again, and put it in an oven, and dry at first at 60° C., and after an hour increase the temperature to 75° C. until well dry, which takes between three to four hours. Transfer the filter with the morphine into a desiccator, let it cool well, and weigh quickly.

It must not be thought that when we obtain the amount of morphine as above from 10 grms. of opium that is the real and true amount of morphine contained in the opium. Here is the point where, perhaps, some of my *confrères* fall into error and give low results in the percentages of morphine in the opium, and no doubt why in most chemical books, in speaking about the Smyrna opium, say that it does not contain more than 10 per cent of morphine when dried and analysed, which brings it down to 8·065 per cent of morphine when fresh, taking into consideration that Smyrna opium contains on an average 24 per cent of water when fresh. Such low percentages are absurd with good qualities of Smyrna opium.

For an example, let me bring here the method used by the British Pharmacopœia (1893) given in the test for opium (pp. 295—297) the following:—"The crystals should weight 10 grains, or not less than 9½ and not more than 10½ grains, corresponding to about 10 per cent of morphine in the dry powdered opium."

And again, the British Pharmacopœia takes 140 grains of dried opium and make their own solutions, and then keep a certain amount of solution, which corresponds to 100 grains of opium, but it seems a rather round-about way; why not take all the amount of opium and exhaust it well? Are they sure that that amount of solution taken represents the 100 grains of opium and not less or more of it?

When the morphine has been weighed and the tare of the filter-paper subtracted, the following calculation must be made in order to find the true amount of morphine, viz., from the time the ammonia has been added to the time of the last washing with water, the number of hours must be counted and the temperature of the day also taken into account. For the following calculation let us take 15° C. as an example, but as the temperature of the day varies with the season, say, 20—25—30° C., the solubility of the morphine is in direct ratio to the temperature; so as many hours as have elapsed the number of hours should be multiplied by the factor 0·004583, which is the morphine dissolved in 100 c.c. of the liquid in one hour's time (if the quantity of the liquid increases so much more per cent of morphine will be dissolved); then the percentages are worked out, and the true amount of morphine is obtained. Because to the watery extract we added alcohol, ammonia, and the water present for the extraction, the morphine which is precipitated on standing for twelve hours is re-dissolved in small quantities, as found by my experiments. This with the amount of water for washings brings it to the factor 0·004583 per 100 c.c. of liquid in one hour's time. For higher temperatures the factor will be as follows:—

20° C.	0·004910
25° C.	0·005237
30° C.	0·005564

and so on.

Therefore taking the watery extract to be 100 c.c. with 30 c.c. alcohol and 3—4 c.c. ammonia, then 50 c.c. water for washings, this would make altogether 184 c.c. of liquid and twelve hours standing at 15° C.

$$\frac{184 \times 0{\cdot}004583 \times 12}{100} = 0{\cdot}10119264,$$

which is the amount of morphine required to be added to the found morphine by weight in the 10 grms. of opium.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, November 18th, 1903.

Prof. W. A. Tilden, D.Sc., F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Allan Baguley, B.Sc., University College, Bangor; James Rocheid Forrest, D.P.H., Kirkee, near Poona, India; Harry James Glover, 33, Albert Road, Stroud Green, N.; John Augustus Goodson, 19, Darnley Road, Hackney, N.E.; Alfred Henry Hoit, 4, Montgomerie Road, Southsea; Bernard Middleditch, B.A., Woodcroft, Harrow-on-the-Hill; Bertram Prentice, Ph.D., D.Sc., Royal Technical Institute, Salford; Frederick Henry Streatfeild, 9, Crescent Road, South Tottenham, N.; William Wood Underhill, 10, Hartham Road, Holloway, N.; Francis Langston Watt, 111, Lauderdale Mansions, Maida Vale, W.

Of the following papers those marked * were read:—

*149. "*The Union of Carbon Monoxide and Oxygen and the Drying of Gases by Cooling.*" By A. F. Girvan.

The following experiments were made in order to investigate whether the drying of an explosive mixture of carbon monoxide and oxygen by exposure to low temperatures was sufficient to prevent chemical union taking place when the gas was sparked after it had regained the ordinary temperature.

A small glass gas-holder containing the explosive mixture was sealed to the following apparatus arranged in series:—(1) A small bubbler containing water, (2) a stopcock, (3) a vertical glass spiral, (4) a glass tube, 1 c.m. in diameter, furnished with platinum terminals with a spark gap of about 4 m.m., (5) a stopcock, (6) a Topler pump. Stopcocks were sealed as side-tubes between (2) and (3), and between (5) and (6). The carbon monoxide was prepared by the interaction of "pure" sulphuric and formic acids, the oxygen being obtained by heating potassium permanganate; the gases were collected and stored over water, and the proportion was correct to within 1 per cent.

A slow current of air was aspirated through the apparatus by means of the side-taps, while the whole apparatus between them was thoroughly heated. The spiral was then surrounded by a freezing mixture, and the tube between it and the pump was heated to the softening point of the glass. After some time, the current of air was stopped and the heating discontinued. The apparatus was then completely exhausted as far as the bubbler by means of the Topler pump, and the explosive mixture slowly admitted at the rate of one bubble per second. When the gas in the apparatus was under atmospheric pressure, the tap of the gas-holder was closed, and sparks from an induction coil

were passed through the explosion tube which the gas was now at the temperature of the atmosphere.

In the first experiments, where liquid air was used, care had to be taken that this cooling agent was not too fresh, as it was then sufficiently cold to liquefy the explosive mixture. No explosion took place on passing sparks from an induction coil which, at the same time, was giving 12 m.m. sparks in the air, although the sparks in the gaseous mixture were usually surrounded with a little ball of blue flame. When the glass spiral was allowed to regain the ordinary temperature, the moisture which had been condensed in the spiral slowly diffused into the explosion-tube, and a single spark exploded the mixture with a sharp report.

On sparking the mixed gases which had been cooled in a mixture of solid carbon dioxide and alcohol (−80°), there was no explosion, and the little ball of flame round the sparks had much the same appearance as when the gases had been dried at −180°, but when the glass spiral had acquired the ordinary temperature, a single spark produced a sharp explosion. When the gaseous mixture had been cooled to −15° and allowed to regain the ordinary temperature, the first spark always caused an explosion, but this did not occur after cooling below −50°. When dried between −50° and −35°, faint sparks did not, as a rule, cause the mixture to explode, although powerful sparks always produced this effect. The freezing mixture employed was either liquid air or solid carbon dioxide in alcohol, and when kept in a vacuum-vessel its temperature arose only about half a degree per minute, even when a current of air was passing through the spiral.

A single powerful spark, when passed through the mixture (after drying between −50° and −35°), frequently produced no effect, whereas an explosion always occurred on passing the second or third spark.

The explosion produced by powerful sparks in the gases dried between −50° and −35° is of a very different character from that obtained with the wet gases; the latter is very quick and violent, and gives a metallic click, but the former takes place quietly, and the explosive wave often travels quite slowly along the tube (compare Dixon, *Phil. Trans.*, 1884, clxxv., II., 630). The wave proceeding from these feeble explosions always stopped directly it reached the cold part of the spiral, and the gas in this part of the apparatus was found to be unaltered, but when the gas was moist and the spiral at the ordinary temperature, the explosion passed to the furthest part of the apparatus.

The platinum terminals were now replaced by (1) a silver wire, (2) a gold wire; each of these was heated to redness and then fused by an electric current, without causing any visible union in the explosive mixture, which had been dried at about −80°. In order to find out whether platinum would act catalytically on the dried or partly dried gases (compare Dixon, *loc. cit.*) a tube, in which the platinum terminals were replaced by a coil of platinum wire, was sealed in place of the sparking-tube, and the apparatus dried as before. The explosive mixture was then allowed to enter through the spiral, which was kept at various temperatures.

With a mixture dried at about −35°, the platinum acted catalytically, and in becoming heated to redness brought about a quiet and feeble explosion. When, however, the mixture was dried at temperatures between −80° and −180°, the platinum still acted catalytically and glowed for several seconds, but there was no other sign of chemical action. After the glowing had ceased, the coil was kept at a white heat for several minutes by means of an electric current, and the gas was then pumped off and collected. About one-eighth of the gaseous mixture was absorbed in caustic potash solution and the residue was still explosive, showing that combination was far from complete.

At Sir William Ramsay's suggestion, the author calculated the amount of moisture present in the mixture after cooling (compare *Trans.*, 1886, xlix., 46), the following data being employed:—

Temperatures ..	−61°	−56·3°	−51°	−45°	−36°
Pressures in m.m.	0·008	0·01	50·029	0·052	0·160

When the vapour pressure of the water is less than about 0·03 m.m., as is the case with the mixture after cooling at −50°, the gases will not explode. When the vapour pressure is less than about 0·16 m.m., the explosion is very feeble.

In the first case, the amount of water vapour present is about one part in twenty-four thousand by volume, and in the second, one part in five thousand. At −61°, the amount of water vapour would be about one part in a hundred thousand of gas.

It would appear then that the mixture will not explode when sparked at the ordinary temperature if there is less than one mol. of water vapour to twenty-four thousand mols. of the gas.

These figures must, however, be taken as being only approximate, since below −50° the vapour pressure of ice falls to half its value for a decrease of about 7°, and, moreover, it is not known whether the glass of the apparatus exerts any drying effect on the contained gas.

Discussion.

Sir W. Ramsay pointed out the interest of Mr. Girvan's experiments in connection with surface-layers on glass. The water vapour in contact with the water-layer on the glass must have a vapour-pressure comparable with, or less than the vapour-pressure in contact with ice at −185°. This film is removed on heating the glass in a current of dry air, and is not removed when the mixed gases, dried at −60°, are allowed to enter the dried tube. Such questions are of very great interest from the standpoint of molecular physics, and Mr. Girvan, he knew, hoped to attack these and similar problems at an early opportunity.

Dr. Scott suggested that the water which adhered to the glass might be there not as a gaseous layer but either as a hydrated silicate or in combination with alkali.

*150. "*Simplification of Zeisel's Method of Methoxyl and Ethoxyl Determinations.*" By W. H. Perkin.

In this process, a long-necked distilling flask was employed without any condensing arrangement, the tube for the current of carbon dioxide being passed down the neck to within a short distance of the hydriodic acid. It was eventually found that as long as the temperature of the glycerin bath was so adjusted that actual distillation of the acid into the delivery tube did not take place, no appreciable quantity of hydrogen iodide passed forward into the silver nitrate flasks. The acid used boiled at 126° and had a sp. gr. of 1·68 approximately.

The following arrangement has been found to prevent the silver nitrate solution from being sucked back into the distilling flask after a sudden ebullition of hydriodic acid. Two small flasks are used as usual, but the tube conducting the carbon dioxide and methyl iodide vapour, instead of passing into the silver solution, is kept some distance above its surface. The flasks are then connected with a syphon tube, one arm of which reaches to within a short distance of the solution in the first flask, whilst the other arm dips a little below the surface in the second. By this arrangement, the methyl iodide is chiefly absorbed by the surface of the silver solution, but any escaping is caught as it bubbles through the second quantity; then, if any such drawing back takes place, some of the solution passes into the first flask, and as soon as the pressure increases is forced back again into the second.

This method of determining the methoxyl group gave very good numbers, and can be used equally well for determining the ethoxyl group, but in this case the numbers are not usually so accurate, being generally a little less than the calculated quantity.

*151. "*The Rusting of Iron.*" Part II. By G. T. Moody.

The author has further investigated the causes of the rusting of iron, more particularly with reference to the influence of soluble substances, and finds that the salts of strong acids, such as sodium chloride and sulphate, potassium sulphate, ammonium sulphate, magnesium chloride and sulphate, calcium chloride and sulphate, and potassium chlorate have no retarding influence on rusting. These

salts do not combine with, and are not decomposed by, carbonic acid. Compounds which inhibit rusting may be divided into two classes. The first contains substances having an alkaline reaction, such as sodium carbonate, hydroxide, phosphate, and borate, ammonium carbonate, and barium and calcium hydroxides, all of which directly absorb and combine with carbonic acid. The second class includes salts of weak acids, such as potassium and sodium nitrites, sodium formate, sodium acetate, potassium ferrocyanide and chromate. These salts are all decomposed by carbonic acid. Sodium nitrite solution, for example, after exposure to air becomes alkaline, and contains sodium carbonate. A solution of 10 grms. of the nitrite, through which a slow stream of carbon dioxide was passed for nine days, contained 1·585 grms. of sodium carbonate. Similarly, potassium ferrocyanide solution, when exposed to air, slowly evolves hydrogen cyanide and becomes alkaline. This change occurs more rapidly when carbon dioxide is passed through the solution, the escaping gas having the odour of hydrogen cyanide and precipitating silver cyanide from a solution of silver nitrate. Potassium ferricyanide is a salt of a weak acid which exceptionally does not appear to retard rusting. This substance is, however, reduced by iron whether its solution be exposed to air or not, the metal becoming covered in either case with a mass of insoluble, greenish-blue cyanide.

It may therefore be concluded that the influence of any particular compound on the atmospheric rusting of iron depends on its behaviour towards carbonic acid, and that only those substances which combine with or are decomposed by carbonic acid inhibit rusting.

Dunstan has stated (*Proceedings of the Royal Artillery Institution*, 1899, v., 26, and *Proc.*, xix., 150) that the metals which rust in air are oxidised by hydrogen peroxide, whilst those which are not oxidised by this reagent do not rust in air. Iron, zinc, and lead are cited as examples of the first class, and copper, silver, and nickel as types of the second. It is noteworthy that iron and zinc rapidly decompose aqueous carbonic acid, whilst copper, silver, and nickel are indifferent to the acid. Having regard to this, and also to the fact that Giorgis (*Gazzetta*, 1891, xxi., 510) has shown that hydrogen peroxide, when carefully freed from carbon dioxide, is practically without action on magnesium, it appeared probable that iron would not be oxidised by pure hydrogen peroxide. The author has investigated this question by leaving a specimen of distilled hydrogen peroxide in contact with iron for fourteen days. No oxidation of the iron was observed, but on adding to a further portion of the pure peroxide containing iron a drop of hydrochloric acid or a solution of carbon dioxide, hydrated ferric oxide was formed.

In the light of the experiments described, the aërial rusting of iron cannot be attributed to hydrogen peroxide, but must be regarded as a change involving the interaction of iron and acid, and subsequent formation of rust by the oxidation of ferrous salt.

DISCUSSION.

Dr. RIDEAL remarked that Müntz had shown (*Comptes Rendus*, 1891, cxii., 1142) that calcium nitrite in sterilised soil gave off nitrous acid rapidly in presence of carbonic acid, and that he had noticed this reaction in bacterial sewage filters.

Mr. W. A. DAVIS pointed out that the decomposition brought about in aqueous solutions of sodium nitrite and potassium ferrocyanide, although at first sight surprising, was a necessary consequence of the principle of mass action. As both nitrous and hydrocyanic acids are volatile, the conversion of their salts into carbonates by an excess of carbonic acid should be complete after a sufficient interval of time.

Dr. MOODY, in reply, said that the sodium nitrite used, which was a well-crystallised specimen, having a high degree of purity and quite free from carbonate, was so sensitive to carbon dioxide that the gas, after passing through the solution, immediately reacted with potassium iodide and starch solution.

152. "*Constitution of Ethyl Cyanoacetate. Condensation of Ethyl Cyanoacetate with its Sodium Derivative.*" By F. G. P. REMFRY and J. F. THORPE.

When ethyl sodiocyanoacetate is heated in alcoholic solution for two hours at 100° with a molecular proportion of ethyl cyanoacetate, a 70 per cent yield of the *compound*, $CN{\cdot}CH_2{\cdot}HC(OEt){\cdot}O{\cdot}CH(CN){\cdot}CO_2Et$, is produced, which crystallises from dilute alcohol in long needles, melts at 53°, and distils with partial decomposition at 235° under 20 m.m. pressure. On boiling with sodium carbonate solution, this substance dissolves, and, on acidifying the solution, the *acid*, $CN{\cdot}CH_2{\cdot}HC(OEt){\cdot}O{\cdot}CH(CN){\cdot}CO_2H$, separates; it crystallises from water in large prisms, and melts at 142° with evolution of carbon dioxide, being converted into a *substance* having the formula $(C_7H_{10}O_2N_2)x$, which crystallises from glacial acid in small, yellow needles having no definite melting-point; on distillation, it gives rise to the *compound*, $CN{\cdot}CH_2{\cdot}HC(OEt){\cdot}O{\cdot}CH_2{\cdot}CN$, separating from absolute alcohol in large prisms melting at 181° and boiling at 208° under 25 m.m. pressure. The same substance is produced quantitatively if the ammonium salt of the acid melting at 142° is distilled under diminished pressure.

Concentrated aqueous potash hydrolyses the substances melting at 53° and 142°, forming malonic acid; the compound melting at 181°, when similarly treated, yields malonic and acetic acids.

When the sodium compound of the condensation product is heated directly with methyl iodide, the *methyl* compound, $CN{\cdot}CHMe{\cdot}HC(OEt){\cdot}O{\cdot}CH(CN){\cdot}CO_2Et$ is produced; it crystallises from dilute alcohol in small prisms, melts at 63°, and boils without decomposition at 220° under 20 m.m. pressure. With sodium carbonate, the *acid*, $CN{\cdot}CHMe{\cdot}HC(OEt){\cdot}O{\cdot}CH(CN){\cdot}CO_2H$, is produced; it crystallises from water in glistening plates, melts at 145° with evolution of carbon dioxide, and becomes converted into a compound, $(C_8H_{10}O_2N_2)x$, having no definite melting-point, but which, on distillation, is converted into the *substance*, $CN{\cdot}CHMe{\cdot}HC(OEt){\cdot}O{\cdot}CH_2{\cdot}CN$, crystallising from absolute alcohol in small prisms, and melting at 121°. The same substance is produced when the acid melting at 145° is boiled for some time with sodium carbonate solution, or when its ammonium salt is distilled. The substances melting at 63° and at 145° give, on hydrolysis with aqueous caustic potash, malonic and methylmalonic acids; the compound melting at 121° yields methylmalonic and acetic acids.

When the sodium compound of the condensation product is treated directly with ethyl iodide, it is converted into the *ethyl* compound, $CN{\cdot}CHEt{\cdot}HC(OEt){\cdot}O{\cdot}CH(CN){\cdot}CO_2Et$, which crystallises from dilute alcohol in prisms, melts at 68°, and boils without decomposition at 215° under 20 m.m. pressure. With sodium carbonate it yields the *acid*, $CN{\cdot}CHEt{\cdot}HC(OEt){\cdot}O{\cdot}CH(CN){\cdot}CO_2H$, which crystallises from water and melts at 153° with evolution of carbon dioxide, and becomes converted into an infusible substance having the formula $(C_9H_{14}O_2N_2)x$. The latter compound, on distillation, gives rise to the substance $CN{\cdot}CHEt{\cdot}HC(OEt){\cdot}O{\cdot}CH_2{\cdot}CN$, which crystallises from absolute alcohol in small plates melting at 115°.

Complete hydrolysis of the above-mentioned substances melting at 68° and 153° gives rise to malonic and ethylmalonic acids; the compound melting at 115° yields ethylmalonic and acetic acids.

When the substance melting at 53° is treated with excess of sodium ethoxide and methyl iodide, it is converted into the *trimethyl* compound, $CN{\cdot}C(Me)_2{\cdot}HC(OEt){\cdot}O{\cdot}CMe(CN){\cdot}CO_2Et$, which crystallises from dilute alcohol in small needles and melts at 120°. Complete hydrolysis of this substance with aqueous potash gives rise to methylmalonic and dimethylmalonic acids.

The action of acidic hydrolytic agents on these substances, and the condition governing the formation of similar condensation products from substituted ethyl cyanoacetates, is under investigation.

153. "*The Action of Water and Dilute Caustic Soda Solutions on Crystalline and Amorphous Arsenic.*" By W. T. Cooke.

Engel (*Comptes Rendus*, 1883, xcvi., 1314) states that amorphous arsenic is unaltered in moist air, whilst the crystalline modification oxidises rapidly. The author's experiments were made with the view of ascertaining:—(1) Whether water alone had any action on either variety; (2) whether the action, if any, was increased by the presence of caustic soda; (3) and whether, in the presence of air, the crystalline variety dissolved to a greater extent in caustic soda solution than in water.

Amorphous Arsenic.—The operations were carried out entirely in an inert atmosphere, the gas employed being either carbon dioxide or hydrogen, according as water or caustic soda solution was used. The main part of the apparatus consisted of two boiling tubes provided with condensers, and also with tubes for the introduction of the gas. Hydrogen arsenide was passed into one carefully dried boiling-tube, so that arsenic was deposited on warming. The water or caustic soda solution contained in the other tube was freed from air by boiling and by passing through it a current of hydrogen or carbon dioxide. The pressure of the gas in the apparatus was then used to force over the solution into the tube containing the arsenic, after any remaining hydrogen arsenide had been expelled. The solution could then be boiled in contact with the arsenic for any desired time, and finally drawn off through an asbestos filter. The arsenic in the filtrate was usually estimated by titrating with iodine solution.

The following results were obtained, using 125 c.c. of distilled water:—

Time of boiling, in hours.	Weight of dissolved arsenic, in grms.
2·5	0·0020
1·5	0·0009
2·5	0·0004
8	0·0034
4	0·0013
6	0·0016

In the absence of air, the action of water on amorphous arsenic is thus seen to be very slight. When air was aspirated through the boiling water for six and one-sixth hours in contact with the amorphous arsenic, only 0·0010 grm. of the element was dissolved, hence the presence of air has no effect.

In the absence of air, the effect of dilute caustic soda solutions was slightly greater than that of water, and the action increases with the concentration of the alkali. Moreover, the action is not influenced by the presence of air.

Concentration.	In the absence of air.		In the presence of air.	
	Time of boiling, in hours.	Weight of dissolved arsenic, in grm.	Time of boiling, in hours.	Weight of dissolved arsenic, in grm.
N/100	1·5	0·0022	2·75	0·0014
	5·3	0·0026	6·0	0·0014
N/50	3·5	0·0021	2·5	0·0038
	6·0	0·0020	6·0	0·0010
N/25	6·0	0·0038	6·0	0·0046
			6·0	0·0014

Crystalline Arsenic.—In this case, the boiling tube was provided with a side tubulure, through which the crystalline arsenic could be introduced. The arsenic was powdered and introduced into the apparatus as quickly as possible on account of the readiness with which the finely-divided element undergoes oxidation. The volume of liquid used was 50 c.c. When distilled water was used and air excluded, about 0·0025 grm. of arsenic dissolved in one-and-a quarter to one-and-a-half hours.

With distilled water in presence of air, about 0·0233 grm. of arsenic dissolved in one-and-a-quarter hours. Hence the presence of air greatly increases the action in the case of the crystalline modification of the element. The following results obtained with caustic soda show that the alkali does not materially increase the action.

Concentration.	In the absence of air.		In the presence of air.	
	Time of boiling, in hours.	Weight of dissolved arsenic, in grm.	Time of boiling, in hours.	Weight of dissolved arsenic, in grm.
N/100	6	0·0025	6	0·0712
N/50	6	0·0016	6	0·0797
N/25	6	0·0030	6	0·0267
	6	0·0017		

By estimating the dissolved arsenic by the iodometric and gravimetric methods, it was found to be entirely in the form of arsenious acid.

The results seem to show that water, either alone or in the presence of caustic soda, has practically no action on arsenic. In the presence of air, however, direct oxidation takes place. If water is concerned in the oxidation, the formation of hydrogen arsenide might be anticipated: $2As+3H_2O=As_2O_3+6H$, $2As+6H=2AsH_3$, but this gas was never found in the foregoing experiments.

Th. Panzer (*Chem. Centr.*, 1903, ii., 821), has also shown that the oxidation of arsenic in moist air is due, not to the decomposition of water, but to the intervention of free oxygen.

154. "*Note on a Double Chloride of Molybdenum and Potassium.*" By G. G. Henderson.

According to Berzelius (*Poggendorff's Annalen*, 1826, vi., 331, 339; vii., 261), a chloride of molybdenum and potassium is obtained when the black liquid produced by the action of potassium amalgam on a solution of molybdenum pentachloride is evaporated to the crystallising point, and is described as a black efflorescent salt, which, when re-dissolved in water, leaves a black powder, probably a basic salt.

A definite *double chloride* of molybdenum and potassium, having the formula $3KCl,MoCl_3,2H_2O$, has been prepared in the following manner:—Potassium amalgam was added, in small quantities at a time, to a solution of molybdic acid in excess of hydrochloric acid until the liquid had acquired a purple-black colour. The solution was concentrated and saturated with gaseous hydrochloric acid, when successive crops of crystals were obtained; the first was composed of potassium chloride alone, the second of a mixture of potassium chloride with red crystals of the double salt, and the third of the double salt alone. The red crystals were collected, washed with fuming hydrochloric acid, dried by pressure between folds of filter-paper, and analysed with the following result:—

Found: Mo = 21·39, Cl = 45·46, H_2O = 7·47.
$3KCl,MoCl_3,2H_2O$ requires Mo = 20·92, Cl = 45·80, H_2O = 7·80 per cent.

The new salt, which crystallises in garnet-red prisms, is fairly easily soluble in cold water, without any apparent decomposition, giving a deep red solution. In the dry state the salt is quite stable, but it decomposes in aqueous solution, slowly in the cold, but quickly on boiling; this decomposition is prevented by the presence of hydrochloric acid. The salt is dissolved to a small extent, by concentrated hydrochloric acid, which then acquires a deep red colour.

When a solution of molybdic acid in hydrochloric acid was reduced in a similar manner by sodium amalgam, a few red crystals were obtained, very similar in appearance to those of the potassium salt; they probably consisted of the corresponding double chloride of molybdenum and sodium, but were not analysed on account of the difficulty of freeing them from admixed sodium chloride.

An attempt was made to prepare the potassium salt by adding potassium chloride to a concentrated solution of molybdic hydroxide, $Mo(OH)_3$, in hydrochloric acid, and subsequent saturation of the liquid with gaseous hydrochloric acid, but in this case the brilliant green crystals of the compound $2KCl,MoOCl_3,2H_2O$, which has been pre-

pared previously, but in a different manner, by Nordenskjöld (*Ber.*, 1901, xxxiv., 1572), were produced instead of the expected double chloride. It was found that the same green crystals could be prepared by the action of potassium amalgam on a solution of molybdic acid in hydrochloric acid, if the potassium was added in smaller quantity than is necessary for the production of the red double chloride, and also that the green salt could be converted into the red salt by reducing its hydrochloric acid solution with potassium amalgam.

155. "*The Action of Benzamidine on Olefinic β-Diketones.*" By S. Ruhemann.

The author showed that hydrogen chloride reacts with a mixture of *m*-nitrobenzaldehyde and a β-diketone to form a *m*-nitrobenzylidenediketone, instead of giving rise to the additive product. Thus, *m*-nitrobenzaldehyde and acetylacetone furnish *m*-nitrobenzylideneacetylacetone, $CAc_2{:}CH{\cdot}C_6H_4{\cdot}NO_2$, melting at 101—102°. The yield of *m*-nitrobenzylidenebenzoylacetone,—

$$PhCO{\cdot}CAc{:}CH{\cdot}C_6H_4{\cdot}NO_2$$

(m. p. 111—112°), is very small, owing to the ease with which it is decomposed by acids. One of the products of the decomposition which has been isolated is *m*-nitrobenzylideneacetophenone, $COPh{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2$ (m. p. 145°).

m-Nitrobenzylidene-β-diketones are also produced by the action of piperidine on the dry mixture of the aldehyde and the diketone. But in alcoholic solution the saturated tetraketone is formed, such as *m*-nitrobenzylidenebisbenzoylacetone, $NO_2{\cdot}C_6H_4{\cdot}CH(CAc{\cdot}COPh)_2$ (m. p. 229—230°).

Benzamidine reacts with benzylidenebenzoylacetone, $PhCO{\cdot}CAc{:}CH{\cdot}Ph$, at the ordinary temperature to form an additive compound (m. p. 132°), the constitution of which is $NH{:}CPh{\cdot}NH{\cdot}CPh(OH){\cdot}CAc{:}CHPh$, because the compound is decomposed by dilute hydrochloric acid, giving rise to dibenzamide. Similar additive products with benzamidine are formed from the other olefinic β-diketones; these, however, are changed when their alcoholic solutions are heated on the water-bath. Thus, sodium ethoxide and benzylideneacetylacetone react with benzamidine at 100° as follows:—

$$CAc_2{:}CHPh + CPh(NH_2){:}NH + C_2H_6O = C_{17}H_{16}N_2 + MeCO_2Et + H_2O.$$

The compound $C_{17}H_{16}N_2$ (m. p. 149—150°) is most probably dihydrodiphenylmethylpyrimidine,—

$$CHMe{<}\begin{matrix}CH{:}CPh\\N{=}CPh\end{matrix}{>}NH.$$

Benzamidine and *m*-nitrobenzylideneacetylacetone interact differently, since *m*-nitrophenylphenylmethylpyrimidine, $N{<}\begin{matrix}CPh{-}N\\CMe{\cdot}CH\end{matrix}{>}C{\cdot}C_6H_4{\cdot}NO_2$ (m. p. 137—138°), is formed, instead of the corresponding dihydropyrimidine. The olefinic monoketone, benzylidenedesoxybenzoin, $COPh{\cdot}CPh{:}CHPh$, does not condense with benzamidine. and the action of hydrogen chloride on the mixture of *m*-nitrobenzaldehyde and desoxybenzoin proceeds in the same way as when benzaldehyde is used, and yields $COPh{\cdot}CHPh{\cdot}CHCl{\cdot}C_6H_4{\cdot}NO_2$ (m. p. 166—167°).

156. "*Dissociation Constants of Trimethylenecarboxylic Acids.*" By W. A. Bone and C. H. G. Sprankling.

In connection with the work on methylenedimethylsuccinic acid, it became necessary to determine the dissociation constants of some trimethylenedicarboxylic acids, since no data with respect to them were available. The following numbers were obtained:—

	K 25°.
Tetramethylenecarboxylic acid	0·00171
Trimethylene-1 : 1-dicarboxylic acid	2·08
cis-Trimethylene-1 : 2-dicarboxylic acid ..	0·042
trans-Trimethylene-1 : 2-dicarboxylic acid..	0·0215

A comparison of these values with those of the corresponding open chain saturated acids containing two additional hydrogen atoms indicates that the formation of a trimethylene ring increases the constant, this effect being particularly noticeable in the succinic series.

157. "*The Elimination of Hydrogen Bromide from Bromo-gem-dimethylsuccinic Acid and from Bromo-trimethylsuccinic Anhydride.*" By W. A. Bone and H. Henstock.

Bromo-gem-dimethylsuccinic acid (m. p. 140°) is readily prepared by heating *gem*-dimethylsuccinic acid with the calculated quantity of dry bromine in sealed tubes at 130—140°; when heated with re-distilled diethyl aniline at 130°, carbon dioxide is freely evolved, hydrogen bromide is eliminated, and *αaα₁α₁-tetramethyldihydromuconic acid* is formed in the following manner:—

$$2CO_2H{\cdot}CMe_2{\cdot}CHBr{\cdot}CO_2H = CO_2H{\cdot}CMe_2{\cdot}CH{:}CH{\cdot}CMe_2{\cdot}CO_2H + 2HBr + 2CO_2.$$

The new acid is obtained in well-defined transparent prismatic forms melting at 70°; it is extremely soluble in the ordinary organic solvents with the exception of light petroleum; its aqueous solutions immediately decolorise alkaline permanganate with formation of the *dihydroxy-acid*, $CO_2H{\cdot}CMe_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CMe_2{\cdot}CO_2H$, which melts at 129—130°. The dissociation constant of the tetrahydromuconic acid is K 25° = 0·001684. The acid distils unchanged under the ordinary pressure, but when boiled with acetic anhydride it yields its own liquid anhydride.

In view of Paolini's observation (*Gazzetta*, 1900, xxx., [2], 497) that ethyl dimethyltrimethylenedicarboxylate is the product of the action of phosphorus pentachloride upon ethyl hydroxytrimethylsuccinate, the authors have repeated the work of Bone and Sprankling on the action of diethylaniline on bromotrimethylsuccinic anhydride (*Trans.*, 1902, lxxxi., 50), and by a study of the physical properties of the resultant acid, $C_7H_{10}O_4$, have fully confirmed the previous conclusion that it is *methylenedimethylsuccinic acid*, $CH_2{:}C(CO_2H){\cdot}CMe_2{\cdot}CO_2H$. This acid melts at 142°, has a dissociation constant K 25° = 0·01597, and gives an insoluble calcium salt. Determinations of the refractive power and magnetic rotation of diethyl methylenedimethylsuccinate, made by Dr. W. H. Perkin, sen., fully support the argument in favour of the unsaturated character as against the "trimethylene" configuration of the foregoing acid.

PHYSICAL SOCIETY.

Ordinary Meeting, November 27, 1903.

Dr. R. T. Glazebrook, F.R.S., President, in the Chair.

Mr. Horace Darwin exhibited an Electric Thermostat.

The thermostat shown at the meeting was made for Lord Berkeley, and is similar to one made for the spectrograph of the 24-inch refractor of the Royal Observatory, Cape of Good Hope. The vessel, the temperature of which is to be maintained constant, is surrounded by oil contained in a bath. In the oil are placed two heating coils, through which electric currents pass. By automatically controlling these currents, the temperature of the oil—and consequently of the inner vessel—is kept very nearly constant. The control is effected by means of a Wheatstone bridge in the outer oil-bath. This bridge has two opposite arms of copper and two of manganin, so that it is only balanced at some definite temperature. Its deviations from balance affect the position of a long horizontal boom attached to the suspended coil of a galvanometer. The position of the boom determines the greater or less descent of a "hit or miss" arm which is periodically raised by a rotating cam, and can only fall to its lowest position when the galvanometer-boom is to one side and allows it to pass; this position of the boom corresponds to a fall of temperature of the controlling-bridge. Thus the position of the "hit or miss" arm at its lowest position depends on the temperature, and it is the variation of this position

which regulates the amount of current passing through the heating-coils. When the "hit or miss" arm is at its highest position the galvanometer-boom is absolutely free to move to its position of equilibrium. We may call the two coils the intermittent and the permanent heating-coils. At every rotation of the cam the "hit or miss" arm is lowered, and if it passes the galvanometer-boom a key is closed and a current passes through the intermittent heating-coil. Thus the frequency of the intermittent current depends on the temperature of the oil-bath. The duration of the time that the key is closed also varies—it may be long or very short. Every time the key is closed a movement takes place which increases the duration of the next closure of the key. The arrangement of the mechanism is such that when the temperature is steady the "hit or miss" arm will pass the galvanometer-boom as many times as it is stopped by it in a given time. The current passing through the permanent heating-coil is also automatically regulated; if there is not enough heat passing into the oil this current is gradually increased. This is done by cutting out resistance-coils which are in series with the permanent heating-coils. The cam which moves the "hit or miss" arm is driven by a worm gear and any suitable motor, and the oil is kept thoroughly stirred by a fan.

Mr. W. C. D. Whetham asked what accuracy was aimed at in the instrument.

Mr. A. P. Trotter said that the use of thermostats would become more and more important with the perfection of thermometers. It was possible to keep a temperature constant within 1/100° C., but it was very difficult to determine the temperature to that degree of accuracy. In high-class resistance measurements with a Carey Foster bridge one of the greatest difficulties was with regard to the temperature, which must not only be constant, but also capable of exact determination. In the constant-temperature room at the Board of Trade Standardising Laboratory the temperature varied by less than ½° C. from day to day, and he would like to know the greatest accuracy obtainable with ordinary devices in such a room before considering the introduction of the complicated instrument shown to the meeting.

The Chairman expressed his interest in the author's communication, and said he had recently been trying to solve a somewhat similar problem by making use of a horizontal boom, attached to the suspended coil of a galvanometer, for making and breaking a current. His object was to regulate a current of the order of 50 ampères. Dr. Glazebrook asked if it was desirable or important to utilise all the adjustments in the instrument.

The Author, replying to Mr. Whetham, said the instrument had been made as sensitive as possible, but he was not aware within what limits it would maintain the temperature of the bath. The thermostat supplied to the Cape Observatory was capable of keeping the temperature within 1/100° C. for a period of eight hours. In reply to the Chairman, he said that when working with small variations of the external temperature it might be possible to dispense with one or other of the adjustments; but when the external variations were large, it was necessary at times to supply a large quantity of heat to the oil-bath, and in order to do this effectually he thought all the adjustments of the instrument were desirable.

A paper "*On the Occurrence of Cavitation in Lubrication*" was read by Mr. S. Skinner.

The experiments described in the paper arose from an observation made when determining the refractive index of a liquid by means of Newton's rings. As Newton showed the rings can be obtained when a liquid is run into the space between the lenses. If when the liquid has been introduced the upper lens be rolled on the lower, the observer sees following the central dark spot a crescent-shaped space, very bright provided the illumination be sufficiently oblique. This is a vacuous or vapour-filled space, for when the motion of rolling ceases the liquid flows into the space and completely fills it. The inflow of the liquid depends in some way on the viscosity, and the effects are more pronounced when a more viscous liquid is used. The most convenient mode of observation is to use a deeply coloured liquid, and to look at the space by transmitted light. The author has found that a convenient liquid is a strong solution of fuchsin in glycerin. This red solution is so deeply coloured that even up to the point where the lenses are nearest some colour shows, and light is only brightly transmitted at the place where there is a break in the liquid. The cavities which are formed must be produced either by splitting the liquid itself, or by tearing the liquid from the glass surface. The effect may be described as a case of "cavitation." Some experiments were made to imitate the actual case of a fully lubricated axle rotating under a bearing. For this purpose, a thick disk with its edge worked to a spherical surface of curvature equal to the radius of the disk, mounted on an axle, was arranged so that the lower part of the disk dipped into an oil-bath, whilst a flat plate of glass rested on the upper edge of the disk. As the disk rotated oil was carried round, so that the point of contact of the disk and plate was maintained copiously lubricated. The disk represented the axle and the plate the bearing on it. What happened on rotation could be observed by looking through the glass plate with a magnifying-glass. It was seen that during motion a cavity was formed on the side where the edge of the disk was moving away from the plate. The size of the cavity depended on the rate of rotation. In ball-bearings completely immersed in oil, the experiments showed that there must be a small cavity near the point of nearest approach of each ball to its neighbour, and also to the surface on which it is running. As the friction of the bearing is the viscous friction of the oil, it follows that the friction must be considerably reduced by the formation of these cavities which are filled with relatively non-viscous vapour. The high lubricating property of oils owes its origin not only to their superior viscosity, but also, possibly, to the facility with which cavities may be formed in them.

The author illustrated his paper by a series of experiments showing cavitation produced by rolling lenses on plates.

Prof. J. D. Everett said it was interesting to note that cavitation had been observed and correctly explained by Newton. He (Prof. Everett) mentioned that a similar phenomenon was exhibited by a steam-roller working on mud, and gave an explanation of the production of pressure and tension respectively in the liquid near the contact of the roller and the mud. If the mud were sufficiently viscid cavitation might occur behind the roller.

Mr. W. A. Price said that the observations of the author could not fail to be of interest to engineers. He asked to what extent cavitation was going on in an ordinary round bearing or in the slide-valve of a locomotive, and suggested that the views of engineers upon the subject of lubrication might require considerable modification in the light of the present paper.

Mr. C. V. Boys expressed his interest in the paper and the experiments shown by the author. He said that like Mr. Price he had been thinking of the influence of cavitation upon machine bearings, but unlike him he had not come to the conclusion that our ideas on the subject should be changed. In the author's experiments cavitation was produced by the approach of two surfaces on one side of their line of contact and their recession on the other side. In the case of a cylindrical bearing the space between the shaft and journal was believed to be completely filled with oil, and if the shaft were truly concentric there would be neither approach nor recession. He thought that in the case of any cylindrical bearing the rate of approach and recession would never be great enough to produce cavitation. The case of ball-bearings, when using a thick lubricant, was different, and cavitation might occur. If it did it would occur behind the point of contact, and although the production of cavitation involved a loss of energy, he questioned whether it did any appreciable harm. Mr. Boys referred to the dendritic patterns formed, when mixing paints, by lifting the muller from the plate, and

suggested that their formation was a phenomenon of the same kind as cavitation.

Mr. R. Appleyard said there were two distinct cases to be considered:—(1) A wheel on a plane, and (2) a shaft in its bearings. He agreed with Mr. Boys that the cavitation occurred behind the point of contact, and did not matter in the case of a ball-bearing. But if cavitation occurred in a cylindrical bearing, the cavity would form between the two surfaces which were next coming into contact. If the surfaces were smooth little harm would ensue, but if they were rough the occurrence of cavitation would be detrimental, for it would result in direct contact.

Dr. A. Griffiths asked the author if cavitation in lubrication was supposed to be an advantage or disadvantage.

Mr. Skinner, replying to Mr. Boys, suggested the construction of glass bearings to determine whether cavitation occurred in cylindrical shafts. He thought that cavitation in lubrication was an advantage as a rule, because spaces formerly filled with viscous material were then filled with something with small viscosity.

Prof. R. Threlfall then exhibited and described the following instruments which he has used in the testing of electric generators by air calorimetry:—

1. A Hot-wire Voltmeter accurate to 1/100th volt. The wire in this instrument is very fine, and special precautions are taken to keep the tension on it constant, so that the elongation measured is due only to the expansion of the wire caused by the heating effect of the current.

2. A Pitot Tube for the measurement of air velocity, the velocity being proportional to the square root of the pressure produced in the tube.

3. A Manometer for determining pressure-differences in Pitot tubes with accuracy. This consists essentially of two bottles containing coloured water, which are connected by a syphon, and the air-space of each bottle is put in communication with its appropriate tube. The readings are taken by setting a pair of needle-points just to touch the liquid surface, and then measuring how they differ in level by micrometer-screws, or by callipering suitable jaws. The instrument is reliable to 0·01 m.m. of water-pressure.

4. A Multiplying Pressure-gauge in which the motion of a float or ball is used to operate a finger moving round a dial. The dial is divided in such a manner that the square roots of the pressure-differences are read off. Air-velocities are therefore given directly.

Mr. Duddell, referring to the voltmeter exhibited, asked if there was any trouble with regard to the temperature variation of the resistance of the wire. In using the instrument with large alternating currents it was necessary to use a standard shunt, and difficulties then arose because of the fact that the self-induction of a shunt, formed of straight bars, and capable of carrying the necessary current, was comparable with its resistance. It might be possible to get a satisfactory shunt by doubling the bars upon themselves to reduce the self-induction.

Prof. Threlfall said that there was no difficulty with regard to changes in temperature of the room because they only altered the zero of the instrument. Referring to the possibility of constructing a low-resistance standard shunt, he said he had calculated the self-induction of the bars forming his shunts, and had come to the conclusion that it was negligible in his experiments. Experimentally he had found that it could not produce an error of 1 per cent. It might be possible to so design a shunt that the mutual induction of its parts would balance the self-induction to a certain extent.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Dr. Andrew Carnegie, Mr. J. S. Curgenven, Dr. J. Emerson Reynolds, and Mr. R. Wissmann were elected Members.

NOTICES OF BOOKS.

A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali. By George Lunge, Ph.D. Third Edition, Revised and Enlarged. Volume I., Parts I. and II., Sulphuric Acid. London: Gurney and Jackson. 1903.

Although only some seven years have elapsed since the appearance of the Appendix to the Second Edition of this work, the rapid development of the subjects of which it treats, especially as regards the manufacture of sulphuric anhydride, has already made it desirable to issue a third edition, which has been re-written to a large extent, and thus, while preserving the essential features of the earlier editions, records the most recent advances and changes which have been made. Certain alterations and omissions have necessarily been made to allow of the inclusion of a large amount of new matter, and many fresh illustrations; while some drawings which appeared in the second edition have not been repeated in order to save space. As the work stands in its present form it undoubtedly represents the most complete treatise of its nature in existence, and it may rightly be regarded as quite indispensable as a work of reference.

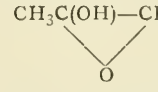
CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 19, November 9, 1903.

Conditions of Separation of Iodine in the form of Cuprous Iodide from a Mixture of Chlorides, Bromides, and Alkaline Iodides.—H. Baubigny and P. Rivals.—The simplest method of separating iodine from a mixture of chlorides, bromides, and alkaline iodides is to precipitate the iodine by the simple addition of $CuSO_4$, and this is really the most effectual if the operation takes place in presence of excess of chlorides and bromides. In no case have the authors obtained an exact result by the method of evaporation *in vacuo* of the liquor and of free iodine, for in this method it seems that after the rough estimation of the iodine remaining in the dry product perfect exactitude is not possible, because when the dry product is dissolved in water, a process which leaves the insoluble Cu_2I_2, a little iodine always goes into solution, and in the form of a cuprous salt, giving a less weight than should be obtained; for example, in a series of experiments on a silver salt, 0·068 grm. AgI were obtained, instead of 0·069 grm., and 0·2742 grm. instead of 0·276 grm.

Action of Organo-magnesium Derivatives on Acetol and its Ether Salts.—André Kling.—The author has previously shown that acetol in solution can exist partially in the form of an ether oxide having the formula—



He now investigates what the constitution of this alcohol and its ethers is in an anhydrous state, and for this purpose he uses organo-magnesium derivatives. When compared with the changes taking place during the reaction of organo-magnesium compounds on epichlorhydrine or on ethylene oxide, he finds that anhydrous acetol or the anhydrous ether salts behave as ketonic compounds and not as internal ether oxide compounds.

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Society of Arts, 8. (Cantor Lectures). "The Mining of Non-Metallic Minerals," by Bennett H. Brough.

TUESDAY, 15th.—Society of Arts, 8. "The British Silk Industry," by Frank Warner.

WEDNESDAY, 16th.—Society of Arts, 8 "The Science of Taxation and Business," by Sir William Henry Preece, K.C.B., F.R.S.

—— Chemical, 5 30. "Relative Strengths of the Fixed Bases and of Ammonia as Measured by their Action on Cotarnine," by J. J. Dobbie, A. Lauder, and C. K. Tinkler. "New Halogen Derivatives of Diphenyl and Dihydroxydiphenyl," by J. C. Cain. "Constitution of Nitric Peroxide" and "Sabatier's Nitrosodisulphonic Acid," by E. Divers. "Notes on some Natural Colouring Matters," by A. G. Perkin and E. Phipps. "Estimation of Methyl Alcohol in presence of Ethyl Alcohol," by T. E. Thorpe and J. Holmes.

LONDON HOSPITAL MEDICAL COLLEGE.
(UNIVERSITY OF LONDON).

LECTURESHIP ON PHYSICS.

The College Board is about to appoint a LECTURER ON PHYSICS. The Lecturer will be required, in addition to teaching Physics for the Preliminary Scientific M.B. London Examination, to assist in the teaching of Chemistry for the same. The Lecturer must be qualified for recognition as a Teacher of Physics by the University of London.

Applications to be sent to the Warden not later than December 31st.

MUNRO SCOTT,
Turner Street, Mile End, E. Warden.

NORTHERN POLYTECHNIC INSTITUTE,
HOLLOWAY, LONDON, N.

The Governors of the above Institute invite applications for the following appointments, to date from January 1st, 1904:—1 Head of Building Trades Department; Salary £250. 2. Assistant in Building Trades Department; Commencing Salary £100. 3 Assistant Lecturer and Demonstrator in Chemical Department; Salary £90. Forms of application, to be returned not later than December 14th, may be obtained from

W. H. MACBETH, Clerk to the Governors.

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2299.

AN EXACT SEPARATION OF CERTAIN OF THE RARE EARTHS.

By G. URBAIN and H. LACOMBE.

Fractional crystallisation of two salts which are not somorphous can never result in the production of either the least soluble or the most abundant in a good state of purity. If the solution has a certain composition to start with, the two salts crystallise simultaneously, forming a eutectic mixture, and never, however often crystallisation is repeated, can they be absolutely separated.

In the case of isomorphous salts the phenomena are quite different. By a series of fractional crystallisations properly carried out a mixture of isomorphous salts can be separated into its constituents in the order of their solubility.

After a sufficient number of fractionations each one will be obtained pure. It will also be noticed, indeed, that in a mixture of isomorphous salts a more soluble member of the series diminishes the solubility of a less soluble member. The true solubility of each salt when in a pure state is profoundly modified by the presence in the solution of an homologous salt of the series in such a manner that during separation by fractional crystallisation the individual solubility of each salt appears of less importance than the tendency of the salts to substitute each other in the crystalline deposit.

It is this tendency to substitute one another in the deposit which enables us in certain cases to separate the least soluble salts in a pure state from those which accumulate in the mother-liquor. So exact is the separation that even the most delicate tests fail to discover a trace of the least soluble salts at the opposite end of the fractionation.

To separate elements whose properties vary very slightly from one member to another of the series, as in the family of the rare earths, this remarkable property of isomorphous salts can be utilised. It is by crystallisations of relatively very soluble salts that the best results are obtained. Double salts, where the differences of solubility between the members are usually greater than those of simple salts, can be most conveniently separated by this method. Fractionation methods are still, and likely to remain for a long time, the only means of which allow of the separation of the rare earths among themselves, Cerium alone has a series of stable higher oxides, which can always be utilised for its separation from other rare earths.

In all cases the great difficulty of fractional methods for the separation of the rare earths is the presence of intermediate portions, which, though they can often be considerably reduced, can never disappear altogether, except in the following case :—When an element, usually separated with no difficulty from the rare earths, presents a case of isomorphism. Also if the solubility of the salt of the common element is intermediate between that of the two members of the series.

An example of such a case is the isomorphism of double nitrate of magnesium and bismuth with the double nitrates of magnesium and the rare earths (G. Urbain and H. Lacombe, *Comptes Rendus*, 1903, vol. cxxxvii., p. 568). In a preliminary examination we compared this bismuth compound with the corresponding salts of the samarium-gadolinium group, and we thought at the beginning of our researches that if we added to the magnesium nitrates of these earths, whose fractionation was described by Demarçay (*Comptes Rendus*, 1896, vol. cxxx., p. 1019; 1901, vol. cxxxii., p. 1484; 1901, vol. cxxxiii., p. 1469) with such brilliant results, a certain proportion of bismuth magnesium nitrate, the element bismuth will, little by little, be inserted between the two rare earths, gradually separating the elements. A simple precipitation by sulphuretted hydrogen will then eliminate the bismuth, and we should obtain a rigorous separation in the rare earth series for the first time.

Experiment has fully confirmed our prediction, and the results obtained have surpassed our expectations.

We have fractionated in presence of magnesium nitrate (1) earths rich in samarium, (2) earths rich in gadolinum In both cases we have added a considerable quantity of bismuth magnesium nitrate to the rare earth magnesium nitrates.

After 35 series of fractionations, each resulting in 16 fractions, we have made the following observations :—Neodymium concentrates at one end, and is only mixed with bismuth.

Samarium comes next. The oxide extracted from fraction 2 shows the slight yellow colouration characteristic of samarium. This colouration diminishes in the following fractions. In the same way the yellow colouration and the absorption spectra of the solution decrease from one fraction to the next. The proportion of rare earths decreases at the same time as the proportion of bismuth increases. In the first experiment with a substance rich in samarium the Fractions 11 and 12 contain no trace of rare earths. In the second experiment, when an earth containing very little samarium was used, Fractions 4, 5, and 6 contain only bismuth. In the following fractions the rare earths appear again, and their proportion increases up to the end of the series, whilst the proportion of bismuth decreases. The solutions show no absorption spectrum except the last fraction, when faint bands of dysprosium may be distinguished. The colour of the oxide starts from white gadolinia up to the last fraction, when the earth is brick-red.

These observations apparently show that bismuth inserts itself between samarium and gadolinium. We are less certain in our experiments on Demarçay's europium. To elucidate this latter point, we are experimenting with a kilogrm. of earths intermediate between samarium and holmium.—*Comptes Rendus*, November 16, 1903, vol. cxxxvii., No. 20.

THE DECOMPOSITION OF CRYSTALLISED SODIUM THIOSULPHATE BY HEAT.

By ARTHUR JAQUES.

When gradually heated, crystallised sodium thiosulphate melts in its own water at 45°,* and gradually loses more or less of its moisture as the temperature rises to 215° C.,* when the whole of the water is driven off. At 220°* it is decomposed, with liberation of sulphur.

The author, however, finds that when the crystallised salt is quickly heated in a test-tube it is decomposed near the hot wall of the tube while the water is still being given off from the mass ; sulphuretted hydrogen is formed in considerable quantity.

It is evident that the hydrogen present in the SH_2 can only have come out of the water, so that the nascent sulphur, together with the reducing influence of the sodium sulphite formed in the decomposition, has been sufficient to break up the water at the temperature of the mixture, thus,—

$$Na_2S_2O_3 + S + H_2O = SH_2 + Na_2SO_4.$$

Sulphur, sodium sulphite, and sodium sulphate are present in the residue.

It is noteworthy that no sulphur dioxide is given off ; so that the presence of the sodium sulphite appears to be necessary for the action to go on, as otherwise the oxygen out of the water would probably unite with the free sulphur which is present in the residue, forming SO_2. (This would, of course, destroy the SH_2).

* Pape, Roscoe and Schorlemmer's "Treatise on Chemistry."

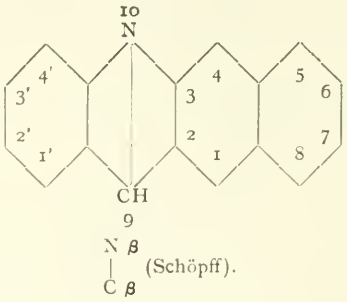
ON ACRIDINES.*

By ALFRED SENIER, Ph.D.,
Professor of Chemistry in Queen's College, Galway.

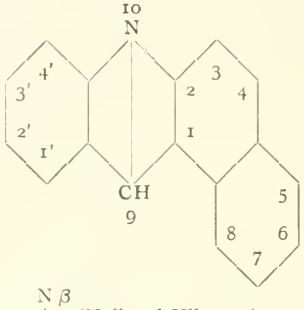
(Concluded from p. 286).

VI. *Phenonaphthacridines.*

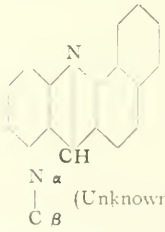
1. *Possible Isomeric Types :—*



N β
| (Schöpff).
C β



N β
| (Nalband-Ullmann).
C α



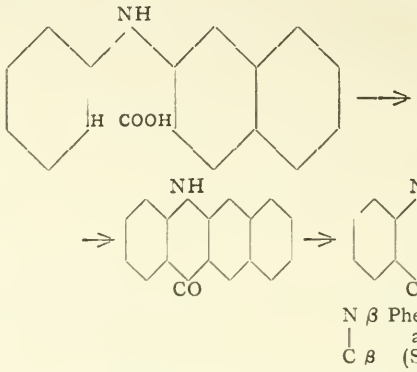
N α
| (Unknown).
C β

The acridine of this type has not yet been obtained, but a corresponding dihydroxyacridone was prepared by Lagodzinski and Hardine (see below).

The naming of the isomerides is a modification of that which I have proposed for the naphthacridines; the numbering is that employed by Ullmann (*Ber.*, 1894, xxvii., 3066).

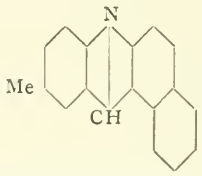
2. *Formation and Constitution :—*

i. The diamine and acid reaction was that first employed. From phenyl-β-naphthylamine and benzoic acid Claus and Richter (*Ber.*, 1883, xvii., 1590) prepared a phenyl-N β | C β -phenonaphthacridine, and Schöpff (*Ber.*, 1893, xxvi., 2589) by a modification of the method, using 2 : 3-anilidonaphthoic acid, obtained the corresponding acridone and acridine, thus :—



N β Phenonaphth-
| acridine
C β (Schöpff).

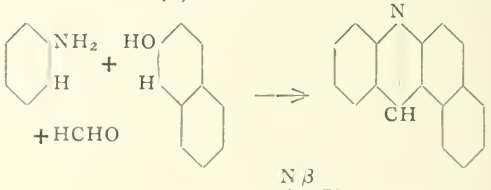
ii. Replacement of one of the naphthalene groups in dihydroxydi-α-naphthyl methane by *p*-toluidine, and subsequent condensation was effected by Ullmann and Naef (*Ber.*, 1900, xxxiii., 905), forming the "leuco" base, phenonaphthacridine dihydride, and by oxidation N β | C α -2'-methyl-phenonaphthacridine :—



Numerous derivatives chiefly of the phenyl ring were prepared (Ullmann and Naef, *Ber.*, 1900, xxxiii., 912 and 2470; Ullmannn and Marié, *Ber.*, 1901, xxxiv., 4320).

iii. Further derivatives of N β | C α phenonaphthacridine were obtained by Ullmann and Naef (*Ber.*, 1900, xxxiii., 916) by replacement of one of the benzene rings in the tetra-amino-ditolylmethane by naphthalene and subsequent condensation.

iv. A modified diamine and aldehyde reaction was also employed by Ullmann and Naef (*Ber.*, 1900, xxxiii., 908). *p*-Toluidine formaldehyde and β-naphthol giving 2'-methyl-N β | C α -phenonaphthacridine. Methods based on this reaction were patented by Ullmann (German Patents 117472, 118439, 123260). The type compound of these derivatives seems to have been first prepared by Nalband (Ullmann and Baezner, *Ber.*, 1902, xxxv., 2671), thus :—

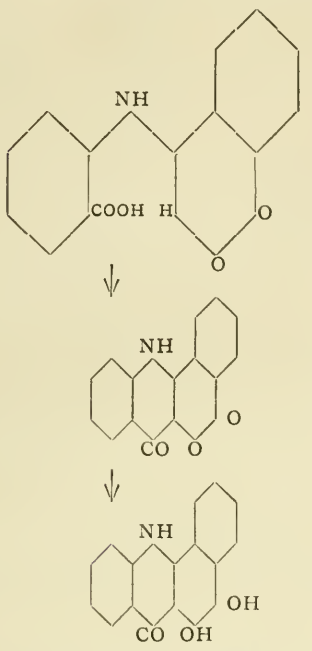


N β
| Phenonaphthacridine
C α (Nalband-Ullmann).

Numerous derivatives are described by Ullmann and his students (*Ber.*, 1901, xxxiv., 4317; 1902, xxxv., 316 and 326; *Journ. Chem. Soc.* Abstracts, 1903, lxxxiv., 447; German Patents 127586 and 128754).

* Abstract of a Paper read before the British Association (Section B), Southport Meeting, 1903.

By this method Lagodzinski and Hardine (*Ber.*, 1894, xxvii., 3068) obtained a dihydroxy-acridone corresponding to the $\begin{matrix} N\ \alpha \\ | \\ C\ \beta \end{matrix}$ type, thus :—



The remarkable readiness with which the acridine grouping is brought about is shown by the recent observation of Ullmann and Baezner (*Ber.*, 1902, xxxv., 2671) that the alcohol group may replace the aldehyde group in this method —that *o*-aminobenzyl, alcohol for example, condenses with β-naphthylamine to form the Nalband-Ullmann base, oxidation taking place during the experiment.

VII. *New Acridines.*

With the assistance of Miss Micklethwait I am now endeavouring to obtain new types of acridines. We are trying by the methylene diiodide and modified diamine method to condense diaminonaphtholenes to form ring of ring compounds; amino-anthracenes to obtain anthracridines, and by means of suitable amino-derivatives to prepare phenoanthracridines and naphthanthracidines. These experiments are in progress, but we are able to announce that in many of them promising fluorescent products have already resulted.

ARSENIDES OF COPPER.

By ALBERT GRANGER.

Chemists who have studied the compounds of copper and arsenic have described a number of these bodies. Gehlen ("Handbuch der Anorganischen Chemie," 6th Edition, vol. iii., p. 702) has prepared a white substance with a metallic lustre, corresponding to the formula Cu_4As_6, by heating a mixture of the two elements. Kane (*Pogg. Ann.*, vol. xliv., p. 471) obtained a black body which should be Cu_3As_2 by reacting with arseniuretted hydrogen on hot chloride of copper, or on sulphate of copper in solution. The reduction of arseniate of copper by cyanide of potassium gives the same body as shown by Descamps (*Comptes Rendus*, vol. lxxxvi., p. 1023). The same worker obtained Cu_3As in a direct manner. These arsenides, Cu_3As_2 and Cu_3As, are produced in the form of metallic ingots, which lose arsenic when they are heated, and leave as residue a less arseniuretted metal, Cu_5As.

By re-melting the product of the reduction of sulphate of copper in solution by arsenic under a layer of boric acid, Descamps obtained Gehlen's arsenide, C_4As_2; he describes it as a crystalline body. Reinsch, by reacting with copper on an arsenious hydrochloric solution, isolated another arsenide, Cu_5As_2, in the form of a grey precipitate.

In nature there are a certain number of minerals consisting of arsenide of copper. Dana ("The System of Mineralogy," 6th Edition, p. 44) describes domeykite, algodonite, and whitneyite, which are arsenides varying from Cu_3As to Cu_6As and Cu_9As. (Koenig (*Bull. de la Soc. Franç de Mineralogie*, 1902, vol. xxv., pp. 266 and 362) has added to this list minerals found in the Mohawk mine at Keweenau (Michigan), and which also contained cobalt and nickel. These arsenides consist of amorphous masses of which the colour varies from white to yellow, and have a metallic lustre.

I have endeavoured to obtain arsenides of copper by direct combination, but I have made use of an apparatus which enables me to avoid too great a superheating, the effect of which is to bring about the partial decomposition of the product formed.

In a glass tube traversing a sulphur bottle, and through which a current of carbonic acid passes, a porcelain boat filled with copper reduced by hydrogen is placed, and in front of it is another boat containing sublimed arsenic. Under these conditions the copper is attacked very easily, and by prolonging the reaction we obtain a well crystallised arsenide, Cu_5As_2, which has the same composition as the body described by Reinsch, but which occurs in very distinct crystals, while the body already described was in the form of an amorphous powder. This arsenide is of a steel-grey colour in the form of octahedra combined with rhomboidal dodecahedra, having cube facets on their summits.

The density of these crystals is 7·56. They gradually become tarnished when exposed to the air, nitric acid dissolves them, and the oxidising agents, chlorine and bromine, attack them with ease.

The arsenide, Cu_5As_2, corresponds to a phosphide of copper, Cu_5P_2, that I have described already (*Bull. Soc. Chim.*, [3], vol. vii., p. 614; *Comptes Rendus*, vol. cxiii., p. 1041). It is similar in its chemical properties, but differs in crystalline form, the Cu_5P_2 being hexagonal. This phosphide is only formed at a higher temperature, about 900°. Like this body the arsenide is decomposed when heated to 1200°, only 20 per cent of arsenic remains. At a higher temperature than that obtained by boiling sulphur in an iron bottle we can still prepare a definite and well-crystallised arsenide of copper, but the operation becomes more delicate on account of the possibility of superheating. If, for any reason, the mass is not always kept in the presence of arsenical fumes, there is a loss of arsenic. Among the workers I have already quoted, Descamps obtained arseniuretted copper, the composition of which corresponded to Cu_3As. It is generally an arsenide of this character that we obtain if we proceed without sufficient precautions.

At the bottom of the porcelain boat we find a brilliant brittle ingot, which differs very little in composition from Cu_3As, if the temperature has not reached 900°. Below this temperature it is still possible to obtain the body Cu_5As_2 if we prolong the action of the arsenic.

The reaction is comparable with that by which we prepare Cu_5P_2 (*Ann. Chim. Phys.*, Series 7, vol. xiv., p. 60); after the apparatus has sufficiently cooled, we find a metallic ingot covered with crystals. There is a difference between these two bodies, and that is that the preparation of Cu_5P_2 is infinitely more delicate than that of Cu_5As_2. It is only within very limited variations of temperature that the phosphite is formed, for below 1000° it

gives bodies containing more phosphorus than Cu_5P_2, such as Cu_2P, Cu_2P_2, while only a single arsenide, Cu_5As_2, appears to be formed at this limit. I have not been able to obtain arsenides corresponding to the above mentioned phosphides richer in arsenic than Cu_5As_2.

By a roundabout method, that is to say, by acting with chloride of arsenic on the metal, or with arsenic on chloride of copper, there is certainly an arsenide of copper formed, but it is no other than the body just described. Further, it is formed under the same conditions of temperature, and in the sulphur bottle the reaction of arsenic on chloride of copper can be easily brought about. This method of working offers no advantages on account of the corrosive action of the chloride of arsenic.

The analytical separation of copper and arsenic leads me to make a few remarks which may not be without value. The general method, that is to say, the separation of the two sulphides by means of sulphide of sodium, offers no advantages, as under these conditions the sulphide of copper is difficult to wash, and may pass through the filter. Fresenius pointed out that the precipitation of the copper in the presence of arsenic may be effected by means of sulphocyanate; in the present case I always found copper in the solution. The simplest method is to precipitate the arsenic in the state of ammonio-magnesian arseniate. The solution of the substance in nitric acid is peroxidised with a few crystals of chlorate of potassium. Neutralise with ammonia and add a sufficient quantity of this reagent to obtain a limpid solution, then precipitate with the magnesian solution.

The precipitate once separated, the wash-waters are evaporated to dryness, and the copper is estimated in the residue in the form of sulphide, after precipitation in the state of sulphide or of sulphocyanate, after expulsion of the ammonia.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 14.

A PARTICULAR PROPERTY OF SOME HYDRATED SALTS.

By A. de SCHULTEN.

A consideration of the salts which form several hydrates shows that, as a general rule, by successive increases of temperature, the hydrate richest in water gives the lower hydrates. To take a few examples, I will mention that the sulphate of magnesium containing 12 molecules of water of crystallisation is transformed, even at a few degrees above freezing, into a sulphate containing 7 molecules; that at 52° this gives the salt containing 6 molecules, and that at 132° this latter forms the sulphate containing only one molecule of water (Gmelin, "Handbuch der Chemie"). The dimagnesian phosphate, $HMgPO_4+7H_2O$, heated to 100°, gives the salt $HMgPO_4+3H_2O$ (*Ibid.*) Carbonate of soda containing 10 molecules of water gives, while efflorescing at 12·5°, the salt containing 5 molecules of water, and the latter when heated to 38° gives the salt containing 1 molecule (*Ibid.*).

There are some series of hydrated salts which form an exception to this rule. All the hydrated salts being so many perfectly distinct compounds, the peculiarity in question is simply an individual property. Nevertheless, it appeared to be interesting to record it in the following well-established cases.

We know two hydrated double carbonates of lime and sodium: gaylussite, $CaCO_3.Na_2CO_3,5H_2O$, and pirssonite, $CaCO_3.Na_2CO_3.2H_2O$. Gaylussite loses the whole of its water at 100°. I have confirmed this fact with well-crystallised, artificial gaylussite prepared according to Fritzsche's method. The loss at 100° was found to be 30·30 per cent (gaylussite contains 30·41 per cent of water).

Pirssonite does not undergo any change at 100°, and it is only at a temperature of 130° that it loses the whole of its water. I have checked the accuracy of these facts by operating on artificially prepared pirssonite, made by the method I have previously described (*Comptes Rendus*, 1896, vol. cxxii., p. 1023).

The artificial pirssonite used for this purpose was very well crystallised and extremely pure, as the following figures, obtained by analysis, show:—

	Found.	Calculated.
Na_2O	25·69	25·65
CaO	23·28	23·13
CO_2	36·21	36·34
H_2O	14·91	14·88
	100·09	100·00

Thus it is well established that gaylussite loses the whole of its water at a temperature at which pirssonite does not undergo any change.

During the course of my research on trimagnesian phosphate and arseniate (*Bull. Soc. Min.*, 1903, vol. xxvi., p. 81) I had occasion to observe that the phosphate, $Mg_3(PO_4)_2+22H_2O$, well-crystallised and pure, when heated to 100°, very quickly loses 18 molecules of water, and then very slowly loses more water, while artificial bobierite, $Mg_2(PO_4)_2+8H_2O$, also well crystallised and pure, does not undergo any alteration at 100°.

The crystallised arseniate, $Mg_3(AsO_4)_2+22H_2O$, loses 17 molecules of water very quickly at 100°, and then slowly a further quantity of water, while crystallised artificial hoernesite having the formula $Mg_3(AsO_4)_2+8H_2O$ does not change at all at 100°.

Thus it is shown that the trimagnesian phosphate and arseniate containing 22 molecules of water retain less than 4 and less than 5 molecules respectively at 100°, a temperature at which the arseniate and phosphate containing only 8 molecules of water do not experience any loss whatever.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 14.

RELATIONS BETWEEN ATOMIC WEIGHTS.

By REGINALD J. HUGHES.

Attempts have often been made to find simple numerical relations between the atomic weights of elements in the same series. For instance, it has been pointed out that the atomic weights of Li, Na, K, Rb, and Cs are nearly in the proportion of 1, 3, 5, 11, and 17, taking 7·7 as the unit. Similarly, the elements in the beryllium and oxygen series have atomic weights which are roughly multiples of 8. But none of these methods give more than approximations which generally seem to imply a margin of error greater than is likely to occur in accurate modern determinations of atomic weight.

The following relations between the numerical values of this function for different elements approach more closely to the experimental values, and are, I believe, new:—

Let us suppose that elements are built up of aggregations of corpuscles, which tend to combine in groups according to a comparatively limited number of types, and that these types are the same as those of the compound radicles of our chemistry, which may, on this view, be termed elements of the next order. The types I shall consider at present are NH_4, CN, CH, and NH. The first two, as is well known, are analogous to sodium and chlorine and their related elements. The group CH resembles in many ways triad nitrogen or phosphorus. This is especially shown in organic compounds, such as the pyridine bases, which are benzenes with CH replaced by N; and the radicle NH behaves in several respects like a carbon atom. Stereochemical work has demonstrated that the four free valencies in the group NR can be typified as arranged in space exactly like those of the carbon atom tetrahedron, and that, conversely, the group CH may be replaced by N.

I must premise that I shall not attempt to explain the change in valency of the phosphorus group to pentad, or of copper to dyad. I believe that to be impossible under our

H .. 1·0075	Na .. .. 23·05	C .. .. 12·00	P .. .. 31·0	V .. .. 51·2	Cl .. .. 35·45
O .. .. 16·000	Cu .. .. 63·6	Si .. .. 28·4	As .. .. 75·0	Nb 94	Br .. .. 79·96
	Ag .. .. 107·93	Ti 48	Sb .. .. 119·9		I .. .. 126·86
	Au .. .. 197·2	Ge 72		Ta 183	
		Zr .. .. 90·6	Bi 208		

present method of regarding valencies. The annexed table shows the elements considered and the values of the atomic weights used, most of which are, I think, in accordance with the best observations.

Suppose $N_1+4H_1=Na$, $N_1+H_1=C$, and $C_1+N_1=Cl$; calculating this out we get—

$H_1=3·683$, $N_1=8·317$, $C_1=27·133$, and $C_1+H_1=30·816$,

the accepted value for phosphorus being 31·0.

Now take $N_2+4H_2=Cu$, $N_2+H_2=Si$, $C_2+H_2=As$; then $H_2=11·733$, $N_2=16·667$, $C_2=63·227$. Hence—

$$C_2+N_2 = 79·894 = Br;$$

the experimental value is 79·96.

Similarly, if $N_3+4H_3=Ag$, $N_3+C_3=I$, $C_3+H_3=Sb$; $H_3=20·194$, $N_3=27·154$, $C_3=99·706$; so that—

$$N_3+H_3 = 47·348 = Ti.$$

The agreement is not quite so good, but the atomic weight of titanium is not very accurately known.

On examining the values found for C_1, C_2, and C_3, it will be seen that—

$$C_1 = 3 \times 9·0443$$
$$C_2 = 7 \times 9·0324$$
$$C_3 = 11 \times 9·0642$$

The values of C increase by a constant amount.

If these are really species of "carbon radicles," and if PH, AsH, &c., are also analogous to carbon, then the latter series might show the same numerical relationship; and this is the case.

$$PH = 3 \times 10·669$$
$$AsH = 7 \times 10·858$$
$$SbH = 11 \times 10·992$$
$$BiH = 19 \times 11·000$$

I only claim that the numbers taken as units are approximately constant; they show evidence of a definite increase at a diminishing rate. There is a missing element at $15 \times 10·996$; this gives $X=163·933$. Now $H_3-H_2=8·461$ (see above), and $H_2-H_1=8·050$. We may take as a hypothesis that the increase is always approximately 8. 24+3·7 gives $H_4=27·7$. Subtracting from 163·933, we have

$$C_4 = 136·233 = 15 \times 9·082.$$

Moreover, H_5 will be about 35·7. Subtracting from Bi (208),—

$$C_5 = 172·3 = 19 \times 9·068.$$

We can now calculate the atomic weight of gold:—

$$N_5+H_5 = Zr = 90·6;$$

so that—

$$N_5 = 54·9 \text{ and } N_5+4H_5 = Au = 197·7.$$

Using germanium in the same way (as N_4+H_4), the missing element between silver and gold would have an atomic weight of 155·1.

The most analogous element to hydrogen in the halogen group is chlorine. PCl, AsCl, &c., might, on my theory, also be species of "carbon radicles," and the same series again appears, the unit being this time still more constant. The value of X is that obtained above.

$$PCl = 3 \times 22·15$$
$$AsCl = 5 \times 22·09$$
$$SbCl = 7 \times 22·19$$
$$XCl = 9 \times 22·15$$
$$BiCl = 11 \times 22·13$$

The appearance of the multipliers 5 and 9 suggested an examination of the vanadium series. The atomic weights of members of this group are, however, not known to a very high degree of accuracy.

$$VH = 5 \times 10·44 \qquad VCl = 4 \times 21·66$$
$$NbH = 9 \times 10·56 \qquad NbCl = 6 \times 21·58$$
$$TaH = 17 \times 10·82 \qquad TaCl = 10 \times 21·84$$

It is difficult to believe that these relations can be all due to coincidence. The method should be capable of wide extension, so as to include eventually all the elements in the table, and also further analyse those whose structures have been tentatively described above. It must be noticed that I do not consider either the series H_1, H_2, &c., or N_1, N_2, &c., to increase by constant increments; but the series C_1, C_2, &c., does increase in an arithmetical progression, like the successive additions of CH_2 to an organic radicle.

Trinity College, Cambridge.

THE DETERMINATION OF POTASH IN FERTILISERS BY SUBSTITUTING MILK OF LIME FOR AMMONIA AND AMMONIUM OXALATE AS THE PRECIPITANT.*

By C. L. HARE.

The Lindo-Gladding method for the determination of potash in fertilisers possesses one particularly objectionable feature: the evaporation and ignition of an aliquot with sulphuric acid for the purpose of expelling ammonia salts and destroying dissolved organic matter is a tedious process, and involves probable loss from sputtering during evaporation. A reliable modification which would exclude this feature would be highly desirable. At the Sixteenth Annual Meeting of the Association of Official Agricultural Chemists Mr. Ross presented a method based upon the use of barium carbonate as a precipitant for phosphates, iron, alumina, &c. He later suggested milk of lime as the precipitant, and the writer, in 1901, reported results obtained by collaborators on official methods for potash determination. The method employed is as follows:—

Weigh out 10 grms. of the sample and boil with about 350 c.c. of water for thirty minutes; while hot, add milk of lime till slightly alkaline. Cool, make up to 500 c.c. with water, and remove 50 c.c., corresponding to 1 grm. Acidify with hydrochloric acid, add platinum solution, and evaporate to soft dryness over water-bath. The residue is then washed with 80 per cent alcohol and ammonium chloride "wash," as in the Lindo-Gladding method.

In the case of fertilisers containing organic matter, treat 10 grms. of sample with dilute sulphuric acid (1 : 1) and incinerate; moisten ignited mass with dilute sulphuric acid (1 : 1), and heat to aid in removing from the dish; boil with 350 c.c. water, and proceed as before. The milk of lime precipitates all lime except that present as sulphate, and the solubility of the sulphate being only 1 in 500, the aliquot of 50 c.c. will contain only 0·1 grm. of that substance, an amount readily removed by the ammonium chloride wash-water, and insufficient to cause material trouble either when solution is made with water direct or after incineration with sulphuric acid.

The potassium platinic chloride crystallises well, and, after washing with alcohol, the salts of lime appear in light flakes, which require never more than six washings with ammonium chloride "wash" for complete removal.

* Proceedings of the Nineteenth Annual Convention of the Association of Official Agricultural Chemists, held at Washington, D.C.

TABLE I.—*Determination of Potash in Fertilisers containing no Organic Materials.*

(Solution by boiling sample with water).

Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.
Per cent.	Per cent.	Per cent.	Per cent.
1·02	1·29	4·11	4·12
1·42	1·62	1·06	1·29
4·51	4·53	3·91	4·02
2·33	2·20	1·96	1·89
1·91	1·91	2·59	2·63
1·97	1·87	2·46	2·48
2·42	2·42	4·36	4·47
1·95	2·12	3·12	2·93
2·54	2·64	2·10	2·08
2·56	2·45	2·52	2·26
2·44	2·36	2·11	2·27
1·09	1·04	2·50	2·76
1·10	0·90	4·37	4·33
2·14	1·89	2·49	2·74
1·75	1·89	1·75	1·89
1·66	1·88	1·95	1·66
1·76	1·88	3·91	3·86
2·59	2·44	1·21	1·44
1·40	1·65	1·50	1·80
0·84	0·80	1·49	1·32
4·33	4·53	5·33	5·65
2·44	2·35	2·16	2·00
2·41	2·35	4·26	4·10
5·24	5·17	2·72	2·76
1·58	1·73	2·49	2·76
2·29	2·08	3·41	3·40
0·81	0·98	2·51	2·67
2·37	2·29	4·21	4·04
3·66	3·90	2·77	2·41
2·44	2·88	2·04	1·88

TABLE II.—*Determination of Potash in Fertilisers containing Organic Materials.*

(Samples treated with dilute sulphuric acid and incinerated prior to solution in water).

Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.
Per cent.	Per cent.	Per cent.	Per cent.
2·16	2·21	1·59	1·57
1·87	1·84	2·73	2·59
2·58	2·53	1·32	1·46
1·71	1·70	2·37	2·10
1·31	1·51	2·71	2·61
2·13	2·24	2·65	2·53
2·27	2·39	2·16	2·20
2·46	2·48	2·61	2·89
1·48	1·49	1·62	1·82
1·35	1·08	2·66	2·42
1·59	1·60	2·38	2·08
2·07	1·80	1·97	1·78
1·51	1·50	1·16	1·20
2·49	2·38	2·44	2·63
2·37	2·60	2·20	2·29
1·92	1·96	3·22	3·11
1·66	1·70	2·21	2·13
2·59	2·45	1·31	1·31
2·33	2·38	2·41	2·28
2·09	2·11	2·28	2·33
2·12	1·96	3·67	3·46
3·46	3·33	3·38	3·36
2·41	1·93	0·74	0·84
2·47	2·50	2·34	2·22
2·46	2·73	2·69	2·60
4·84	4·69	2·43	2·44
2·53	2·57		

TABLE III.—*Determination of Potash in Fertilisers containing Organic Materials.*

Lime Method.—Samples ignited before solution.
Lindo-Gladding Method.—Unignited sample boiled with water.

Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.
Per cent.	Per cent.	Per cent.	Per cen .
1·62	1·66	4·00	3·87
2·02	2·19	0·50	0·69
2·14	2·11	2·18	2·47
0·88	0·74	1·18	1·20
1·11	1·06	1·96	1·73
1·82	1·55	1·78	1·68
1·53	1·68	2·00	2·07
1·61	1·63	2·09	2·35
3·09	3·02	1·52	1·62
1·84	2·06	1·80	1·78
2·05	2·10	2·17	2·25
2·43	2·32	1·62	1·70
2·52	2·65	1·65	1·71
2·95	2·86	2·38	2·43
2·00	2·29	1·83	1·64
1·95	2·03	2·63	2·37
1·92	2·11	2·88	2·60
2·58	2·74	2·24	2·21
2·38	2·23	2·97	2·94
1·92	2·09	1·43	1·26
2·71	2·64	1·95	2·06
1·56	1·34	1·84	2·14
1·98	1·96	1·93	2·14
1·15	1·28	2·37	2·56
2·28	2·54	1·65	1·81
1·29	1·53	3·70	3·46
2·53	2·29	3·41	3·52
1·32	1·28	1·54	1·30
2·26	2·07	1·35	1·48
1·50	1·49	2·68	2·80
1·88	1·60	2·85	3·13
2·94	3·00	3·03	3·02

TABLE IV.—*Determination of Potash in Fertilisers containing Organic Matcrials.*

(Samples boiled with water).

Lime method.	Lindo-Gladding method.	Lime method.	Lindo-Gladding method.
Per cent.	Per cent.	Per cent.	Per cent.
1·27	1·21	2·35	2·49
1·04	1·15	2·50	2·05
2·71	2·61	2·69	2·31
1·34	1·16	2·15	2·18
1·74	2·06	1·54	1·17
1·38	1·21	1·95	2·04
2·87	2·44	2·57	2·35
2·65	2·35	2·50	2·24
2·28	1·83	2·19	2·14
2·50	2·54	2·11	2·11
1·28	1·25	1·16	1·20
2·41	2·14	2·43	2·45
1·43	1·08	1·29	0·99
1·79	1·71	2·17	2·24
5·51	5·51	5·85	5·56
5·03	4·61	2·16	1·87
2·01	1·92	2·30	1·83
2·48	2·18	2·43	2·09
2·70	2·20	2·40	2·25
2·64	2·40	1·00	1·10
3·42	3·38	2·41	1·93
2·53	2·42	2·30	2·10
2·23	1·80		

The modification possesses several advantages over the Lindo-Gladding method :—(1) The precipitation of lime is immediate, and there is no delay at this point ; (2) evaporation to expel ammonia salts is eliminated ; (3) probable

loss of potash during evaporation is obviated; (4) washing the potassium platinic chloride with alcohol and ammonium chloride "wash" may be performed thoroughly with greater ease and rapidity, while no larger amount of platinum is required than by the Lindo-Gladding method.

The accuracy of the method is evidenced by results, as shown in the tables. It has been used by the writer upon several hundred samples of miscellaneous fertilisers as a check against the Lindo-Gladding, and it is evident that the modification would not be applicable to fertilisers containing ammonia salts.

Table I. gives parallel results by the milk-of-lime and the Lindo-Gladding methods upon fertilisers containing no organic materials, solution in each case being made by boiling the sample with water.

Inspection of the tables reveals differences ranging from 0·01 to 0·27 per cent, with two exceptions, in a total of 60 samples. Of this number 46 show differences less than 0·20 per cent, while the average difference is 0·10 per cent.

This average difference is, of course, without value as an indication of accuracy, unless considered in connection with the variation of each parallel determination, but when so large a percentage of duplicates falls within the limits of probable error the average in differences of the entire number of determinations indicates in a measure the comparative accuracy of the two methods.

Considering that the figures in the tables represent first results, and in no case a second determination by the same method, results by the milk-of-lime method appear quite as reliable as those obtained by the Lindo-Gladding method. In the regular course of laboratory work, duplicate determinations by one and the same method may easily show less closely agreeing results.

Table II. shows parallel results obtained from fertilisers containing organic materials, the samples in each case being treated with dilute (1 : 1) sulphuric acid and incinerated before making solution in water.

By reference to Table II., we find variations ranging from 0·01 to 0·48 per cent in a total of 53 determinations. Forty-one of these give differences of 0·20 per cent or less, results averaging 0·06 per cent higher by the lime method than by the Lindo-Gladding.

Table III. contains results from fertilisers containing organic materials. Samples were ignited with sulphuric acid (1 : 1) before obtaining solutions for the lime method; while for the Lindo-Gladding, solution was obtained by boiling the unignited sample with water.

These results show an extreme variation of 0·29 per cent in a total of 63 determinations. Forty-six of the 63 vary less than 0·20 per cent, while the results average 0·02 per cent lower by the lime method.

In Table IV. may be found results on fertilisers containing organic materials, solutions of both methods being obtained by boiling the sample with water. The solutions for the lime method were considerably coloured by dissolved organic matter.

Although little was expected from the results obtained by the lime method under these conditions, still they show an extreme variation of only 0·55 per cent in a total of 45 determinations, while 30 of the 45 differ less than 0·30 per cent, and the average difference is only 0·15 per cent. Nothing is claimed for the method when used under these conditions, but it is interesting to note that the method gives many good results, even when precipitation of platinum takes place in a solution considerably coloured with organic matter.

Analysis of Steel Works Material.—M. Beranger has made arrangements with Messrs. Longmans, Green, and Co. for the issue of a French translation of Brearley and Ibbotson's "Analysis of Steel Works Materials."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, December 3rd, 1903.

Prof. W. A. Tilden, D.Sc., F.R.S., President, in the Chair.

Messrs. M. Kemp-Welch and J. T. Ainslie Walker were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Alfred Denys Cowper, 3, Bishop's Mansions, Fulham, S.W.; Nevil Norton Evans, McGill University, Montreal, Canada; John Monteath Guthrie, 199, Ferry Road, Leith, N.B.

The President announced that since the last meeting a photograph of the portrait of Roger Bacon, which is in Knole House, had been presented to the Society by Mr. Oscar Guttmann.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Robert Duncombe Abell, Ph.D., D.Sc.; Percy Appleyard; Edward F. Armstrong, Ph.D.; Herbert Henry Ashdown; Herbert Moore Attwell; William Cornish Badcock, B.A.; Harold James Bailey; Thomas Vipond Barker; Harold Goodenough Bayly; Charles Marsh Beadnell; William Beam, M.A., M.D.; Henry James Wheeler Bliss; Nicholas John Bluman; Paul Brühl; Erasmus Robert Buggé; William Clacher; William Thomas Deeks; Ernest Derwent; Henry Russel Ellis; Charles E. Fawsitt, Ph.D., B.Sc; William Forster; John Albert N. Friend, M.Sc.; Ernest A. Gardiner, B.A.; Frank Brooks Gatehouse; Percy William Gent; Frank Barnes Grundy; John T. Hall; Harold Montague Heasman; Arthur V. Hendrickson; John George Howarth; Edwin Reginald Hughes; Herbert Hymans; Edward Charles Ibbotson; William Henry Jackson; Walter Ernest Jennings; Thomas Oliver Kent; John J. Kielty; Thein Kin, B.A.; Harley Fancutt Knight; John Laing; Francis E. E. Lamplough, B.A.; Henry William Lawrence; Harold Duff Leadbetter; Gervaise Le Bas, B.Sc.; David Baird Macdonald; Frederick William McMahon; Ernest William Mann; Gordon W. Monier-Williams, B.A.; Urban Orlando S. Nairne; James Victor Nevin; William Parry, B.Sc.; Henry George Pike; George Horace G. Plymen; William Branch Pollard, B.A.; Mata Prasad, M.A.; Herbert Stanley Redfern, B.Sc.; Stiles William George Rich; Harold E. Richardson, B.A., B.Sc.; Philip Wilfred Robertson; William David Rogers; George Senter, Ph.D., B.Sc.; Arthur Slator, Ph.D., M.Sc.; Frank Gurney Smith; William Veysey Smith, B.A.; Alfred Walter Stewart, B.Sc.; Arthur Tighe; Arnold Turner; William Ernest S. Turner, B.Sc.; Miles Walker-Pole; Carl Friedrich R. Weiss, Ph.D.; Fred Wright.

Of the following papers those marked * were read:—

*158. "*The Molecular Formulæ of some Fused Salts as Determined by their Molecular Surface Energy.*" By J. F. Bottomley.

The electrolytic conductivity of fused salts has not been satisfactorily explained, but it might be expected that ionisation would be produced by the presence of complex molecules, and, at Sir William Ramsay's suggestion, measurements of the variation of the capillary rise with temperature were undertaken with the object of testing this point. The determinations with lithium and silver nitrates, potassium chlorate and dichromate, zinc and stannous chlorides were unsatisfactory owing to experimental difficulties, and successful results were obtained only with sodium and potassium nitrates. The average value of K for sodium nitrate is 0·503, and for potassium nitrate 0·445, instead of 2·12, the normal value for non-associating substances. This implies that 9 or 10 molecules of the simple salt, $NaNO_3$ or KNO_3, are associated to form a complex, the supposition that a portion of the salt is ionised by the complex molecules of another portion being therefore rendered probable.

*159. "*The Atmospheric Corrosion of Zinc.*" By G. T. Moody.

The recorded observation that hydrogen peroxide may be detected during the oxidation of zinc in presence of water has been brought forward by Dunstan in support of his contention that, in the case of iron, hydrogen peroxide "is a necessary intermediate product of the chemical change involved in rusting" ("Report of the Steel Rails Committee of the Board of Trade, 1900; *Proc.*, xix., p. 152). It consequently appeared of interest to determine if the scale formed during the atmospheric corrosion of zinc showed a composition which would justify the assumption that it is to be regarded as an oxidation product formed by the interaction of metal, water, and oxygen. To this end, strips of thin sheet zinc were suspended in a muslin bag under the shelter of a north wall, and exposed to the full effects of the atmosphere for five months. At the end of this period, the semi-crystalline scale was detached from the metal and dried; it had a composition closely agreeing with the formula $ZnCO_3,3Zn(OH)_2$. The production of this basic carbonate may be regarded as evidence that the atmospheric corrosion of zinc is to be attributed not to direct oxidation of metal, but to an interaction with carbonic acid. This view is supported by the behaviour of zinc in a saturated solution of carbon dioxide. The metal dissolves with evolution of hydrogen and formation of zinc hydrogen carbonate. The resulting solution, when heated or exposed to air, becomes turbid, and on spontaneous evaporation yields a basic carbonate agreeing in composition with the product of atmospheric corrosion.

Whilst zinc is rapidly converted into hydroxide by commercial hydrogen peroxide, this metal, like iron, remains practically unattacked when in contact with pure 30 per cent peroxide. The statement made by Dunstan (*loc. cit.*) that iron, zinc, and lead behave similarly towards hydrogen peroxide, is not in agreement with the observations of the author, who finds that the addition of a few m.grms. of assay lead induces immediate decomposition of 30 per cent peroxide, oxygen and steam escaping with almost explosive violence. The lead becomes superficially coated with brown peroxide, and presents an appearance quite different to that arising from atmospheric corrosion.

The author concludes that the atmospheric corrosion of zinc, like that of iron, is the result of interaction between metal and acid, and that the attack on zinc is less marked because the acid is in a great measure retained in combination as basic carbonate.

*160. "*The Formation of Urea by the Direct Hydrolysis of Lead Cyanate.*" By A. C. Cumming.

Lead cyanate is readily and quantitatively transformed into lead carbonate and urea by direct hydrolysis with boiling water: — $Pb(CNO)_2+2H_2O = PbCO_3+CON_2H_4$. This salt, which is prepared by adding lead nitrate to potassium cyanate solution from which the carbonate has previously been removed by barium nitrate, is fairly stable at the ordinary temperature, and may be washed with cold water until free from impurities.

The progress of the change was followed qualitatively with a polarising microscope, advantage being taken of the fact that the small acicular crystals of lead cyanate which polarise light are gradually replaced by amorphous granules of lead carbonate.

The action was also followed quantitatively by a titration method which depends on the fact that lead cyanate neutralises twice as much acid as the products of its hydrolysis.

No evidence was obtained of the formation of ammonium cyanate, and this method is therefore distinct from any earlier synthesis.

Discussion.

The President expressed surprise that this reaction had not already been observed, remembering the use of lead cyanate in a process introduced many years ago by the late Mr. John Williams for the manufacture of urea (*Journ. Chem. Soc.*, 1868, xxi., 63).

161. "*Acid Salts of Monobasic Acids.*" By R. C. Farmer.

The substituted benzoic acids have the general property of forming salts containing one molecule of the free acid to one molecule of neutral salt. The potassium and ammonium salts were taken as typical, and the acid salts of benzoic acid and its methyl-, hydroxy-, bromo-, and nitro-derivatives were examined. These substances form well-defined, crystalline compounds, which do not undergo any change at the melting-points of the free acids; they are not affected by inert solvents, but are at once decomposed by water. Experiments on the ratio of distribution of the acids between benzene and aqueous solutions of their normal salts showed that these acid salts do not exist to any appreciable extent in aqueous solution. In alcohol, on the other hand, the dissociation is only partial, as was shown by molecular weight determinations at the boiling-point.

162. "*The Solubility Curves of the Hydrates of Nickel Sulphate.*" By B. D. Steele and F. M. G. Johnson.

The solubilities of the hydrates of nickel sulphate have been determined at temperatures ranging from $-5°$ to 99°, and equilibrium curves have been constructed for the following hydrates:—$NiSO_4,7H_2O$, $NiSO_4,6H_2O$ (blue quadratic), and $NiSO_4,6H_2O$ (green monoclinic). A fourth hydrate is deposited from saturated solutions at temperatures above 118°, and the salt separating at 131° has been analysed and found to be the dihydrate, $NiSO_4,2H_2O$.

The following quadruple-points have been fixed:—1. The cryohydrate-point of the heptahydrate ($-4·15°$). 2. The transition-point (31·5°): $NiSO_4,7H_2O \rightleftarrows NiSO_4,6H_2O$ (blue) + saturated solution. 3. The transition-point (53·3°): $NiSO_4,6H_2O$ (blue quadratic) $\rightleftarrows NiSO_4,6H_2O$ (green monoclinic). The transition-point of the change: $NiSO_4,6H_2O \rightleftarrows NiSO_4,2H_2O$ + saturated solution, has not been determined.

163. "*Action of Malt Diastase on Potato Starch Paste.*" By B. F. Davis and A. R. Ling.

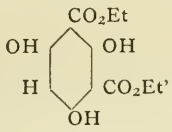
In continuing their earlier experiments (*Journ. Fed. Inst. Brewing*, 1902, viii., 475), the authors show that a solution of diastase, when heated above 55°, becomes weaker in its action, and that the alteration produced in the enzyme molecule is a permanent one, for the diastase retains its acquired properties when it is reprecipitated from its solution by alcohol, and allowed to act on starch paste at or below 55°. The altered diastase produces *d*-glucose when it acts on starch paste, and the change appears to commence when a solution of the enzyme is heated below 60°, although, judging from the small amount of *d*-glucose produced, the reaction is not complete at this temperature. As the temperature of the initial heating is raised, the amount of *d*-glucose produced by the enzyme also increases, the maximum amount being obtained by the action of diastase, which has been previously heated in solution at 68—70° for fifteen to thirty minutes. Above this temperature, the destruction of the enzyme is so rapid that a much larger proportion has to be employed to attain that stage of the reaction at which *d*-glucose appears. Nevertheless, *d*-glucose is formed by diastase which has been heated to 78°, and probably at even higher temperatures. It has been observed in all cases that when the solution is kept at the temperature of hydrolysis (usually 55°) after the maximum amount of *d*-glucose has been formed, the amount of this sugar present diminishes, and the occurrence of this apparent condensing action of the enzyme may probably in several cases explain the failure to detect *d*-glucose among the products of hydrolysis. The maximum amount of *d*-glucose formed in any case does not exceed about 12 per cent of the total hydrolytic products.

164. "*The Formation of Phloroglucinol by the Interaction of Ethyl Malonate with its Sodium Derivative.*" By C. W. Moore.

In the year 1885, Baeyer made the important discovery that when ethyl malonate is heated with its sodium derivative at 145°, a derivative of phloroglucinol is formed,

which melts at 104°, and which Baeyer considered was ethyl phloroglucinoltricarboxylate, $C_6(OH)_3(CO_2Et)_3$ (*Ber.*, 1885, xviii., 3457).

During the course of an investigation involving the use of ethyl malonate, the author was led to re-investigate this matter, and he has been able to prove that the substance formed under the conditions employed by Baeyer is ethyl phloroglucinoldicarboxylate, $C_6H(OH)_3(CO_2Et)_2$, and not the above-mentioned tricarboxylate. The molecular weight determination in benzene solution gave 273 and 270, whereas the molecular weights of the dicarboxylic and tricarboxylic esters are 270 and 342 respectively. The determination of the ethoxyl groups, which was carried out by Dr. W. H. Perkin, sen., also gave numbers which clearly show that the substance is a dicarboxylic ester. When treated with bromine, it yields a bromide having the composition $C_6Br(OH)_3(CO_2Et)_2$, which was first prepared by Bally (*Ber.*, 1888, xxi., 1770). Since it also yields a triacetyl compound when heated with acetic anhydride, there can scarcely be a doubt that Baeyer's ester must be represented by the formula—



and that it is therefore *ethyl phloroglucinoldicarboxylate*.

PHYSICAL SOCIETY.

Ordinary Meeting, December 11, 1903.

Mr. James Swinburne, Vice-President, in the Chair.

A paper on "*A Method of Mechanically Reinforcing Sounds*" was read by the Rev. T. C. Porter.

If a tuning-fork be sounded and placed in a flame, there is a very marked reinforcement of the sound. This is proved not to be due to resonance in the ordinary sense, but to the change from continuous to intermittent combustion. Under certain circumstances the impulses given to the air external to the flame, by the waves of burning gas, are more forcible than those given by the unaided sounding body. Thus a new way of reinforcing the sounds given by a vibrating body is found; and the rest of the paper demonstrates this for the phonograph, a *flame* being used instead of the ordinary *trumpet*. Coal-gas and air are brought by tubes into the chamber of the "reproducer," and thence to a jet, where they are burnt. The vibrations of the reproducer are thus impressed on the issuing gas and air, which burn synchronously with them, the sounds thus emitted being easily heard over a large room. In practice it is found best to spread out the flame by a second jet of air, or of mixed air and gas, placed close to the first jet and at right angles to it. The author describes the nature and quality of the sounds emitted by the flame, and the modifications of these which may be produced. If the first jet is used alone, and a common blowpipe-flame obtained from it, it is found that the sound is markedly reinforced by introducing a thin sheet of platinum foil near the blue tip of the inner cone. This reinforcement is attributed to the rapid expansion and contraction of the platinum in response to the variation in the heat of the flame caused by the sound-waves from the phonograph, and not to simple reflection of these waves from the platinum surface.

The Chairman read a letter from Mr. Chichester A. Bell expressing his interest in the subject of Mr. Porter's paper, and pointing out that the whole matter had been described by him at length in a paper on "The Sympathetic Vibrations of Jets" (*Phil. Trans.*, 1886).

Mr. W. Duddell suggested that the flame was in a condition of instability, so that any disturbance created in it tended to increase in amplitude. If the energy for the increased sound came from the tuning-fork, and the flame simply acted as a trumpet, then the forked would be rapidly damped; but if the flame was unstable the tuning-fork would not be rapidly damped. He asked the author if he had tried experiments on this point.

Prof. A. S. Herschel referred to the ways in which energy could be transmitted by a gas (1) by a flow and (2) by the passage of undulations. The second method was concerned in the experiments shown by the author. In reply to a question by Prof. Ayrton he said he did not think that the increased sound was due to an increase in the amplitude of vibration of the tuning-fork.

Mr. D. J. Blaikley asked if the flame could be so adjusted as to restore a wave-form having a complicated distribution of upper partials, or whether it could only reinforce pure tones. (The Chairman pointed out that in the experiments shown with the phonograph the distinctive character of the notes emitted by the various instruments could be easily recognised).

Prof. H. L. Callendar referred to Prof. Dixon's experiments on the propagation of explosive waves through gases. These waves had been photographed, and proved that the passage of a detonation-wave through an explosive mixture caused a local heating, shown by a corresponding brilliance in the photograph. Complicated effects were produced by the meeting of a detonation- and a retonation-wave, but in every case there was an increase of chemical action in the flame. He suggested that the behaviour of the platinum foil in the blowpipe jet might be ascribed to the meeting of two such waves.

Mr. Porter, replying to Mr. Duddell, said a tuning-fork was unquestionably rapidly damped when placed in a flame. With regard to Prof. Callendar's observations, he said he had looked in vain for anything corresponding to the existence of loops or nodes in the flame. Referring to Mr. Blaikley's remarks, he said that a small flame reinforced the high notes better than the lower ones, and *vice versâ*.

A paper on "*The Simmance-Abady 'Flicker' Photometer*" by Messrs. Simmance and Abady was read by Mr. Simmance.

The principle of the flicker photometer, discovered by Prof. O. N. Rood ten years ago, has frequently been remarked on, but attempts to design a reliable apparatus depending upon this principle have hitherto been unsuccessful. The authors, guided by the following rules, have designed a photometer which is capable of balancing and comparing the most violently contrasted tints:—The light effects must be in juxtaposition without any apparent division line, and must move, oscillate, or rotate so that the point of juncture of the rays of the two lights passes and returns entirely across the vision-field. Any hiatus, or longer exhibition of one light than the other, biasses the result. The observation surfaces, or surfaces upon which the light rays fall, must be at exactly the same distance from the eye, at exactly the same angle in relation to the line of sight, and must be of pure white, such as is afforded, for example, by a clean chalk, plaster-of-Paris, magnesium carbonate, or barium sulphate; any tint affects the accuracy of the result. The observation surfaces must also themselves in turn occupy the field of vision; an apparent movement or optical illusion does not afford accurate results.

Observations made with the photometer, by operators suffering from colour-blindness, astigmatism, &c., make it certain that the relative intensities of two lights, whether of the same colour or different, *can* be accurately and easily gauged by the method. The authors submit that the Purkinje phenomenon does not affect the accurate working of the instrument, as it is a purely colour effect, and colour does not enter into consideration in this photometer. The photometer itself consists of a wheel of a white material with a specially shaped periphery, which wheel is caused to revolve before an eyepiece by means of a suitable motor. At right angles to the line of sight, and parallel with the axis of the revolving wheel, are the two lights undergoing examination, the rays of which fall upon the shaped periphery of

the wheel, enabling the effect of each light to be seen in turn through the eyepiece.

Prof. W. E. Ayrton said it was an important question to settle exactly what the photometer measured. The fact that different observers using the same photometer obtained the same results for the ratio between two lights did not prove that the instrument actually compared intensities. He had come to the conclusion that when the distances between the sources of light and the photometer were great the results were not affected by the Purkinje effect.

The Rev. T. C. Porter expressed his interest in the instrument, and said there was no doubt that the flicker photometer measured intensity independent of colour. The results obtained directly from a flicker photometer agreed with those deduced by indirect methods from observations with ordinary instruments.

Mr. L. Gaster expressed his admiration for the photometer, and explained that this type of instrument was becoming more important because of the great number of improvements made during the last few years in the manufacture of incandescent lamps and arc-light carbons by the addition of other substances to the pure carbon. A great step towards the simplification of the process of photometry had been attained by Prof. C. P. Mathews, by the aid of whose photometer one is enabled to get in one reading an illumination upon the screen, proportional to the mean spherical intensity of the source.

Dr. W. Watson said the authors had compared a red light with a white light, and also a blue light with a white light. He asked if they had compared a red with a blue directly, and if so, how the results agreed with those deduced from the comparison of both with a white light.

Mr. W. Duddell asked what was meant by the equality of two lights of different colours. Was it judged by the eye, the bolometer, or the flicker effect? On account of the Purkinje effect the inverse square law could not be used, and he asked for the real fundamental relation underlying the use of the instrument.

Mr. J. Abady, replying on behalf of the authors, said the discussion had turned mainly on two points:—(1) Does the instrument measure candle-power? and (2) is it independent of the Purkinje effect? If a Bunsen disc were taken and used to compare the candle-powers of two lights of the same colour, the grease-spot vanished at a certain point. If a flicker photometer was substituted for the Bunsen disc, the flicker disappeared at the *same* point. In both cases candle-power had been measured. In reply to Prof. Ayrton he said that results obtained from the photometer by different observers agreed among themselves and also agreed with results obtained from the Bunsen disc photometer. With regard to the Purkinje effect, he did not think it affected the readings of a flicker photometer, because the same values for the ratio between the intensities of two different coloured lights were obtained by varying the distances of the lights from the instrument within wide limits. Answering Dr. Watson, they had carried out the experiments suggested, and the results from the direct and the indirect comparison were in absolute agreement.

Mr. Rollo Appleyard exhibited a Conductometer, the theory and mechanical details of which are fully described in the *Proceedings of the Institution of Civil Engineers*, vol. cliv., Session 1902-3, Part IV.

Prof. L. R. Wilberforce exhibited a Model to illustrate various Properties of Wave-motion.

The model consists of a series of brass balls suspended in a line by spiral springs and capable of transverse or up and down motion. The balls can be set in vibration by releasing them from extreme positions by means of triggers, one set of triggers controlling the up and down motion, and another set the pendular. If the vertical and transverse periods are unequal, the release of the triggers in rapid succession produces a disturbance similar to that produced by the passage of light through a crystal. If the periods are nearly equal effects are shown similar to those observed with Lissajous figures. If the balls are joined together by horizontal springs, condensations and rarefactions can be exhibited. If two of the balls near one end are constrained to move up and down only, and two near the other end are constrained to move transversely, the phenomenon of polarisation can be illustrated. If the balls are put in neutral equilibrium, by supporting them on the upper ends of vertical rods, when suspended by spiral springs which very nearly balance their weights, the reflection of both transverse and longitudinal waves at surfaces of infinite and zero density can be illustrated. By substituting, for some of the vertical rods, vertical rectangular frameworks with heavy pendulum-bobs hanging from the upper sides, the phenomenon of anomalous dispersion can be exhibited.

NOTICES OF BOOKS

Liquid Fuel and its Combustion. By Wm. H. Booth. Westminster: Archibald Constable and Co., Ltd. 1903.

The first part of this book deals with the theory and principles of the subject, and the second with their application to practice. This latter part describes in detail the various systems adopted in using liquid fuel at sea, for stationary purposes and for locomotives; the Holden system as used by the Great Eastern Railway naturally occupies an important place, but those employed in other countries are not by any means neglected. The analysis of flue gas is discussed in a chapter which has been revised by Mr. Horace Allen. The author in the preface has forestalled the obvious criticism regarding the omission of the consideration of some aspects of the subject which might have been expected to be found in such a treatise, and possibly the requirements of readers will justify his selection in most cases; the practical impossibility of including in one volume the description of all methods of utilising liquid fuel will explain the selection of types only of apparatus. The earlier part on the theory and principles is less satisfactory. Some elementary details, which, moreover, hardly seem to have much bearing on the subject, are treated in a misleading manner, as in the pages dealing with heat and temperature, and nowadays it can no longer be stated as an axiom that the scientific man rejoices at the inutility of the discovery he has made. Judging by this specimen of what results when those to whom science is "less familiar, but more attractive," step into the breach caused by the neglect of important industrial methods by scientific men, their efforts are not likely to be attended with enough of success to make it appear advisable to recommend the practice to others in the same category.

Manuel Guide de la Fabrication du Sucre. ("A Manual on the Manufacture of Sugar"). By R. Teyssier. Paris: C. Naud. 1903.

This handbook does not aspire to be a complete treatise on the manufacture of sugar, but aims at describing in as simple language as possible the ordinary appliances to be found in a factory, with the methods of using them, and the means generally adopted to obviate difficulties and remedy accidents. The chemistry of the process receives only very meagre attention, and the book will be found more useful by foremen and works managers than by chemists. The advice and hints given are all thoroughly practical, and the author has evidently had considerable experience in the management both of workmen and machinery. A great deal of the matter, however, would seem to be better and more easily learnt in the factory itself than from the best text-book ever written, though, on the other hand, a good many useful suggestions might be gathered from the pages which deal with the building of an ideal sugar plant

and its management. An appendix of very elementary mathematical results seems somewhat out of place in such a book, but the other tables are very full, and will be constantly found useful for reference.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Edited by Franz Hofmeister. Band IV. 9-11 Heft. Braunschweig: Friedrich Vieweg und Sohn. 1903.

The first article of this issue deals with the important question of the conditions of action of the fibrin ferment and its bearing on the coagulation of the blood. The author, Dr. P. Morawitz, adopts Alexander Schmidt's views, and endeavours to explain the discrepancies between them and those of later investigators; but he cannot be said to have done very much towards the elucidation of this obscure problem, though he has apparently subjected it to a careful investigation. Another interesting paper, by Dr. Otto von Fürth, describes researches on the behaviour of the oil in seeds during germination; in the course of the experiments it was hoped that some light would be thrown on the transformations which fat undergoes in the animal body. Although this hope was not realised the results of the experiments, which were carried out with the seeds of helianthus and ricinus, are very interesting. Most of the other papers are mainly concerned with physiological questions, and are not of much interest to the chemist.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 20, November 16, 1903.

New Preparation of Argon.—H. Moissan and A. Rigaut.—The authors have already proved that the metal calcium combines easily with nitrogen at a dull red heat, giving a crystalline nitride of formula Ca_3N_2. As metallic calcium possesses also the property of fixing hydrogen at the same temperature, giving a crystalline hydride of formula CaH_2, and this hydride does not dissociate at 500°, they now apply these different properties of calcium for the extraction of argon from the atmosphere. The process consists of four operations:—(1) The preparation of 100 litres of nitrogen; (2) the gradual enrichment of the argon in the nitrogen; (3) The first purification; (4) a second purification of the argon by circulation over calcium.

Exact Separation of certain of the Rare Earths.—G. Urbain and H. Lacombe.—(See p. 295).

Acetylenic Acetones. New Method of Synthesis of the Isoxazols.—Ch. Moureu and M. Brachin.—The authors have previously established the fact that the acetones with acetylenic function R—C≡C—CO—R' give, on reaction with the hydrazins, pyrazols identical with those from which the β-diketones are derived on hydration. They now investigate the action of hydroxylamine on the same compounds, and find that isoxazols are obtained, the yield being quantitative.

Retrogradation of Amidon Starch.—L. Maquenne.—In a preceding research the author showed that amidon starch retrogrades with time; that is to say, becomes in part insoluble. This transformation is subordinate to a large number of independent variables, such as temperature, the nature of the medium, concentration, &c. He now investigates the influence of temperature and of the mineral acids employed in sufficient quantity to start saccharification. He finds—(1) That retrogradation is more rapid and complete as the temperature is lower; (2) the phenomenon is assisted by the presence of mineral acids, even in so small a proportion as 1/10,000th; (3) it tends towards a limit, which in a neutral medium at 0° appears to be about 30 per cent.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution before Easter:—

A Christmas Course of Lectures (illustrated by lantern slides and adapted to a juvenile auditory) on "Extinct Animals," by Professor Ray Lankester. To be delivered on the following days at 3 o'clock:—Tuesday, Dec. 29, Thursday, Dec. 31, 1903, and Saturday, Jan. 2, Tuesday, Jan. 5, Thursday, Jan. 7, Saturday, Jan. 9, 1904.

Professor L. C. Miall, Fullerian Professor of Physiology, R.I., six lectures on "The Development and Transformations of Animals."

Mr. E. Foxwell, three lectures on "Japanese Life and Character."

Dr. E. A. Wallis Budge, two lectures on "The Doctrine of Heaven and Hell in Ancient Egypt" and "The Books of the Underworld."

Mr. G. R. M. Murray, three lectures on "The Flora of the Ocean."

Mr. A. D. Hall, three lectures on "Recent Research in Agriculture."

Professor H. L. Callendar, three lectures on "Electrical Methods of Measuring Temperature."

Mr. Sidney Lee, two lectures on "Shakespeare as Contemporaries knew him."

Mr. J. A. Fuller-Maitland, three lectures on "British Folk-Song" (with vocal illustrations).

Mr. W. L. Courtney, two lectures on "Comedy—Ancient and Modern."

The Right Hon. Lord Rayleigh, six lectures on "Physics."

During the Season 1904 the lectures on Tuesdays and Thursdays will be delivered at 5 o'clock, and the Saturday lectures at 3 o'clock.

The Friday Evening Meetings will begin on January 15, when a Discourse will be delivered by the Right Hon. Lord Rayleigh on "Shadows." Succeeding Discourses will probably be given by the Rev. Walter Sidgreaves, Mr. D. G. Hogarth, Mr. Alfred Austin, the Dean of Westminster, Mr. H. Brereton Baker, Mr. Alexander Siemens, Professor W. Stirling, Professor F. T. Trouton, Mr. Henry Arthur Jones, Professor Dewar, and other gentlemen.

The Electrolytic Preparation of Free Periodic Acid.—E. Muller and O. Friedberger.—The authors electrolysed a solution of iodic acid with an anode covered with PbO_2. To estimate the HIO_4 formed, in the presence of the remaining HIO_3, they neutralised with soda until phthalein took a rose colour, added CO_3NaH and KI, then with a titrated solution of As_2O_3 they estimated the iodine set at liberty; the weight of oxygen fixed by the As_2O_3 is a quarter of that contained by the HIO_4. As for the total oxygen of the iodic and periodic acids, it is estimated by means of $S_2O_3Na_2$ in solution acidulated with sulphuric acid and treated with potassic iodide. The preparation of HIO_4 is effected in a small cell in which the porous pot contains the solution of HIO_3 at 50 per cent, and an anode formed of a lead tube, traversed by a stream of cold water if necessary, and having its surface covered with a layer of electrolytic PbO_2. The outer vessel contains a bi-normal solution of sulphuric acid, and a cathode consisting of two sheets of platinum. The details of the experiments will be found in the original paper; in one of them, after four and a-half hours electrolysis with a current of 2 ampères and 6 volts, equal to a density of current of 28 ampères per square c.m., the oxidation was complete. The solution in the porous pot is slightly brown and

cloudy in appearance; it is diluted considerably, filtered, and concentrated on the water-bath; on cooling it then gives large crystals of HIO_4 containing a little sulphuric acid; these can be purified by draining and re-crystallisation. Bromic acid does not give BrO_4H under the same conditions.—*Berichte*, vol. xxxv., p. 2652,

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THE CHEMICAL NEWS.

Vol. LXXXVIII., No. 2300.

FLUORIDE OF GOLD.*

By VICTOR LENHER.

Inasmuch as fluorspar is frequently associated with gold in nature, and quite notably so in the deposits of the telluride ores, it has seemed important to study gold fluoride in order to determine, if possible, whether this substance can play any part in the genesis of these deposits.

The known compounds of gold with the halogens chlorine, bromine, and iodine, are, as a rule, fairly well defined. In the trivalent condition, gold forms the relatively stable chloride, while the bromide and iodide show greater tendency to break down into the lower state of valence of gold.

The halides in which gold shows a monovalence have received considerable attention, and it is known with a reasonable degree of certainty under what conditions aurous chloride, bromide, and iodide are capable of existence.

While the chlorides, bromides, and iodides of gold have received more or less study, comparatively little is known of fluoride of gold. Prat (*Comptes Rendus*, lxx., 843) has prepared an intermediate oxide of gold, Au_2O_2 by the incomplete solution of gold in aqua regia, in which the hydrochloric acid is in excess, treating the solution with sufficient potassium bicarbonate to dissolve the precipitate formed, and warming the clear orange-yellow solution to 95°, when a dark olive-green precipitate was obtained which, when dried, showed the composition Au_2O_2. In studying the properties of this oxide, Prat states that hydrofluoric acid combines with it but without dissolving it. In his study of the action of fluorine on the various metals, Moissan states that at a red heat, gold is attacked by fluorine gas, a yellow hydroscopic substance being formed, and that this substance is readily decomposed into gold and fluorine.

These two experiments give practically what is known of the fluoride of gold.

The activity of the halogens toward other elements is, as a rule, inversely proportional to their atomic weights. The first member of this group of active elements, fluorine, is certainly the most active of all the elements, be they halogens or not; yet, as will be demonstrated later, it appears to have little if any affinity for gold.

In studying the chemistry of gold, it should always be borne in mind that it is the most inactive of the metals, but the relative stability of the most of its salts, notably with the halogens, would appear to make probable the relative stability of the compound of the most active of the elements, fluorine. On the other hand, we have the marked difference of fluorine from the other halogens in the insoluble fluorides of calcium, strontium, and barium, as contrasted with the very soluble chlorides, bromides, and iodides; and the soluble fluorides of silver and thallium as compared with the insoluble chlorides, bromides, and iodides.

In order to study the relations between fluorine and gold, experiments were conducted with the view of bringing about, if possible, the formation of gold fluoride under various possible conditions.

The first experiment made was a study of the action of hydrofluoric acid on gold oxide. To this end, gold oxide was prepared by the action of magnesium oxide on a solution of gold chloride, and the excess of magnesia removed with nitric acid. The gold oxide thus obtained was finely divided, and hence in the most suitable condition to be susceptible to any chemical action. This gold oxide can remain in contact with hydrofluoric acid indefinitely, or, as has been the case, can be boiled for weeks with either hydrofluoric acid alone, or with a mixture of hydrofluoric and nitric acids, without suffering any change whatever. These experiments have been repeated several times, but in no case has gold been found to enter into solution, nor has it been possible to detect fluorine in the precipitate. It is obvious that gold fluoride cannot be prepared by the action of hydrofluoric acid on the oxide. The next most natural method to try for the preparation of the fluoride would be that of double decomposition.

Silver fluoride and gold chloride, both being soluble salts, on being brought in contact in solution should yield theoretically $AuCl_3+3AgF=AuF_3+3AgCl$. The actual case is that when solutions of these two salts are brought in contact, gold hydroxide is quantitatively thrown out of solution along with silver chloride; thus, $AuCl_3+3AgF+3H_2O=3AgCl+Au(OH)_3+3HF$. The accuracy of this reaction has been carefully established in the laboratory.

If gold fluoride is even momentarily formed, it is immediately decomposed by water.

The method yet remaining for the preparation of a substance incapable of existence in presence of water would be the use of anhydrous solvents. A large number of organic solvents have been tried with this end in view, but no substance has been found which would dissolve both gold chloride and silver fluoride; either these salts are insoluble or are decomposed by the substances worked with. Among the solvents examined, mention may be made of the following:—Alcohol, ether, carbon bisulphide, benzene, turpentine, pentane, hexane, chloroform, carbon tetrachloride, ethyl nitrate, nitrobenzene, ethyl acetate, ethyl propionate, and pyridine,

It thus appears that gold fluoride is incapable of existence not only in presence of water, but under the ordinary conditions met with in the laboratory and in nature.

* Read before the Wisconsin Academy of Science, December 26, 1902, and published in the *Transactions*. From the *Journal of the American Chemical Society*, xxv., No. 11.

A PROBABLE CAUSE OF THE DIFFERENT COLOURS OF IODINE SOLUTIONS.

By ARTHUR LACHMAN.

It is a well known fact that solutions of free iodine have different colours, depending in some way upon the nature of the solvent. Gautier and Charpy (*Comptes Rendus*, 1890, cx., 189; cxi., 645), who investigated this problem about twelve years ago, distinguished four sets of colours, of the following types:—

(1) Violet, *e.g.*, chloroform; (2) red, *e.g.*, ethylene bromide; (3) red-brown, *e.g.*, toluene; (4) brown, *e.g.*, alcohol.

A large number of solvents were thus classified, but the authors confessed themselves unable to find any relations between the chemical function of the solvent and the colour. The following year, Rigollot (*Comptes Rendus*, 1891, cxii., 38) determined the absorbing power of different iodine solutions for definite light waves; but his results led to no explanation. A few years later, an elaborate study of the problem was undertaken by Krüss and Thiele (*Zeit. Anorg. Chem.*, 1894, vii., 25). They ascertained the molecular weight of iodine in various solvents, and found that practically in all cases, where moderately dilute solutions were taken, the iodine molecule consists of 2 atoms. Variations from this value were irregular, both for brown and for violet solutions. Concentrated solutions usually gave high molecular weights, indicating association, but no change of colour accompanied this association.

In spite of these results, Krüss and Thiele attempt to explain the different colours by an assumption of different molecular weights: violet solutions containing I_2, brown

solutions $(I_2)_n$, n being greater than 1. These complicated molecules, however, are supposed to give a normal molecular weight by all osmotic methods. This explanation is equivalent to saying that in brown solutions the molecular weight of iodine is much greater than in violet, but that none of our present methods are able to demonstrate the increase; and it involves a conception of the molecular theory whose utility yet remains to be shown. The change from brown into violet is ascribed to dissociation; if the above theory is correct, solvents with brown colour should have less dissociating power than those with violet. But this is contradicted by well-established facts; alcohol has much greater dissociating power than chloroform or benzene.

Notwithstanding the negative results of Gautier and Charpy, and of Krüss and Thiele, a simple causal connection seems to exist between the chemical behaviour of the solvent and the colour of iodine solutions. This relationship was not apparent to the above investigators *because in critical cases they observed wrong colours*, owing to impurities in the solvents. From the table given below, it will be seen that iodine solutions, when made with pure solvents have but two colours—violet and brown—with but one exception, which will be discussed below.

Colour of Iodine in Various Solutions.

A. *Violet Solutions.*

Hydrocarbons:—
- Hexane.
- Benzene (thiophene free).
- Toluene (*a*).
- *o*-Xylene (*b*).
- *m*-Xylene.
- *p*-Xylene.

Halogen compounds:—
- Chloroform.
- Ethylene chloride (*c*).
- Ethylidine chloride.
- Tetrachlorethylene (*d*).
- Carbon tetrachloride.
- Isobutyl chloride (*e*).
- Amyl chloride.
- Chlorbenzene.
- Benzalchloride.
- Benzotrichloride.

———

- Bromoform
- Ethylene bromide (*e*, *f*).
- Trimethylene bromide.
- Amyl bromide (*e*).
- Brombenzene.

Nitro compounds:—
- Nitroethane.
- Nitropropane.
- Tetranitromethane.
- Isobutyl nitrate.

Sulphur compound:—
- Carbon bisulphide

Notes.

(*a*) Gautier-Charpy, red-brown.

(*b*) Thiel-Krüss, wine-red; (xylenes not separated).

(*c*) Gautier-Charpy, Krüss-Thiel, red.

(*d*) Tetra-chlorethylene, C_2Cl_4, is the only substance in the above list which is unsaturated in structure. Its easy formation during chlorination reactions indicates that its unsaturated character is more formal than real, in spite of its double bond.

(*e*) Ethylene bromide, amyl bromide, and isobutyl chloride required careful purification before giving violet solutions. The impure solvents, which gave red solutions, all decolorised permanganate.

(*f*) Gautier Charpy, Kruss-Thiele, red.

B. *Brown Solutions.*

Iodides:—
- Ethyl iodide.
- Amyl iodide.
- Cetyl iodide
- Phenyl todide
- Potassium iodide } In water solutions.
- Hydrogen iodide }

Oxygen compounds.

Alcohols:—
- Methyl alcohol.
- Ethyl alcohol.
- *n*-Butyl alcohol.
- Dimethylethyl carbinol.
- Heptyl alcohol.

Ethers:—
- Ethyl ether.
- Dimethyl acetal.
- Anisol.
- Phenetol.

Ketones:—
- Acetone.
- Methylethyl ketone.
- Diethyl ketone.
- Acetaldoxime.
- Acetophenone.

Acids and esters:—
- Formic acid.
- Acetic acid.
- Lactic acid.
- Caproic acid.
- Ethyl acetate.
- Amyl acetate.
- Isobutyl isobutyrate.

Sulphur compounds:—
- Amyl mercaptan.
- Thiophene.

Nitrogen compounds.

Nitriles:—
- Acetonitrile.
- Propionitrile.
- Capronitrile.
- Benzonitrile.

Nitrilo-bases:—
- Pyridine.
- Quinoline.

From the results tabulated above, all of which have been verified personally, the relationship between colour and the constitution of the solvent stands out clearly; *saturated solvents give violet, solvents which have unsaturated character give brown solutions.* In the first, or violet class, we find hydrocarbons, their chlorides and bromides, and carbon bisulphide; and also, strange to say, the *nitro compounds*. All the other oxygen compounds, so far as investigated, give brown solutions. The brown solvents comprise the alcohols, ethers, ketones, acids, and esters; nitriles and nitrilo-bases; alkyl and other iodides; and bivalent sulphur compounds.

The iodine molecule, as found in iodine vapour, is violet; we have every reason for assuming that in its violet solutions iodine is in a state of normal physical distribution. On the other hand, certain of the brown solutions are known to contain periodides, usually of the form $(MX).I_2$; among these are potassium iodide, phenyl iodide, and the tertiary bases. Nitriles have long been known for their additive properties in general; and in the case of oxygen compounds, the recent startling results of Baeyer and Villiger (*Ber. d. Chem. Ges.*, 1901, xxxiv., 2679) have fully demonstrated the hitherto unsuspected additive powers of combined oxygen atoms. It seems quite justifiable to assume in all brown iodine solutions the existence of (probably unstable) addition products whose general composition is—

$$\text{Molecule-solvent} + I_2.$$

Such an explanation was indeed offered some years ago by Beckmann (*Zeit. Phys. Chem.*, 1889, v., 76), and considered and rejected by Krüss and Thiele. If it is assumed, as it was by Beckmann, that the *whole* of the iodine thus adds to the solvent, the effect upon the *observed* molecular weight would be a marked decrease (as a consideration of Raoult's formula shows), contrary to the measurements of Krüss and Thiele. But there is no need to make this assumption; a very small amount of alcohol suffices to change the colour of an iodine-chloroform solution, and 3 per cent of alcohol gives as dark a brown as can be obtained with pure alcohol.

Effect of Absolute Alcohol on Colour of Iodine in Chloroform.

Alcohol, per cent.	Colour.
3·5	Brown
0·4	Red
0·2	Mixed red and violet
0·1	Violet

The iodine in brown solutions is therefore probably in a condition of equilibrium between pure solution and the addition product—

$$\text{Solvent} + I_2 \rightleftarrows (\text{Solvent} + I_2),$$

very much like many double salts, or like the chlorine ions in green chromium chloride hexahydrate (Werner, *Ber. d. Chem. Ges.*, 1901, xxxiv., 1579).

The view here presented, that brown solutions contain some addition product, and violet solutions simple iodine molecules, is borne out by an important fact:—Brown solutions tend to become violet when heated, and conversely, violet solutions become brown on being cooled sufficiently (Krüss and Thiele, *Comptes Rendus*, 1891, cxii., 72; Gautier and Charpy, *Comptes Rendus*, 1890, cxi., 645; Wiedemann, *Wied. Ann. Phys.*, cclxix., 580). As heat produces dissociation, and cold induces association, the facts are in excellent agreement with expectation.

The actual isolation of the addition products of iodine with oxygen compounds will probably be difficult, but an effort in this direction will be made as soon as possible. Schützenberger has described an addition product of bromine and ether, and iodine may behave similarly (*Comptes Rendus*, 1873, lxxv., 1511; *Liebig's Ann. Chem.*, 1873, clxvii., 86).

Two points remain for discussion. In the first place, the behaviour of the nitro compounds seems to put them apart from other oxygen compounds. The structure of the nitro group is still uncertain, but numerous reactions show that its oxygen atoms are quite active, and possess considerable additive power (Lachman, *Am. Chem. Journ.*, 1899, xxi., 443; *Journ. Am. Chem. Soc.*, 1901, xxiii., 897; Angeli, *Ber. d. Chem. Ges.*, 1896, xxix., 1884; Meisenheimer, *Liebig's Ann. Chem.*, 1902, cccxxiii., 205). Their indifference to iodine will be investigated more closely later on.

The second point is the behaviour of ethyl bromide towards iodine. In spite of numerous efforts, I have not been able to prepare this substance in a state sufficiently pure to obtain with it a violet iodine solution; in every case the solution is dark red. Ethyl bromide is made by two methods; the distillation of ethyl-sulphuric acid with potassium bromide also forms ether, which cannot be separated by the most careful fractioning; and the action of phosphorus bromide upon alcohol yields ethyl bromide contaminated with phosphorus, which resist hours of boiling with moist sodium amalgam. I am confident, however, that ethyl bromide will prove no exception to the above classification of iodine solvents, for similar difficulties were met, during this investigation, with amyl bromide and ethylene bromide. The first samples of these substances gave dark red iodine solutions, but after careful purification pure violet solutions were obtained.—*Journal of the American Chemical Society*, xxv., No. 1.

A GLASS-BLOWING "WRINKLE."

By F. S. LOCKE, M.A., M.D.

Instead of using cork or rubber stoppers, or the cotton-wool plugs often improvised, for temporarily closing the ends of glass tubes requiring to be *blown*, I have for the last couple of years employed plugs formed as required of loose asbestos, which must be of the kind commercially known as "woolly." The proper amount for the particular case is rolled into a ball between the finger-tips and stuffed into the opening to be stopped with the aid of, *e.g.*, a wooden match. The same asbestos can, of course, be used over and over again.

A much better seal is obtained—owing to the adhesive and cohesive quality of this material—than with cotton-wool, which it equals in ease of hasty application. Its unique advantage is the absence of all decomposition, blackening, charring, and consequent cracking, even when the glass is heated close to the plug.

I find that Threlfall ("Laboratory Methods," London, 1898, p. 27) recommends the employment of asbestos for annealing, but does not refer to the application of it here in question.

THE ELECTROLYTIC ESTIMATION OF SMALL QUANTITIES OF SILVER IN THE PRESENCE OF A LARGE AMOUNT OF LEAD.

By MM. ARTH and NICOLAS.

The separation of lead and silver in nitric solution has been described already by several writers, notably by M. Luckow and by M. Riche. We know that lead is generally deposited in the oxidised form on the anode, and that the silver is obtained in the metallic state on the cathode.

We have taken up the examination of this question from a special point of view, which does not seem to have been studied yet, viz., the endeavour to determine the most favourable conditions for the easy estimation of small quantities of silver in the presence of large amounts of lead, and also to determine the limits to which the operation can be carried in a practical manner.

Lead is not deposited in the metallic form on the cathode in a solution containing sufficient free acid, and to be precipitated in the form of the binoxide on the anode a large amount of free acid is necessary, and a fairly high electromotive force.

Silver, on the other hand, only requires moderately acid solutions and a relatively low electromotive force for its deposition. It has, however, the very inconvenient tendency of being deposited in the spongy form, which can only be avoided with certainty by not exceeding a certain voltage, as was shown by Kuster and Steinwehr for the separation of silver and copper, in which case 1·38 volts is the maximum to be used (*Zeit. für Electrochemie*, 1897-1898, p. 451). These two properties are fortunately concordant. It was obviously necessary to try and find if there was any definite electromotive force which would conveniently precipitate the silver contained in a solution of nitrate of lead, while leaving the latter metal intact.

After several attempts, we have decided definitely on a maximum tension of 1·1 volt. With 1·2 volt we can already detect the presence of a few grains of spongy metal on the edges of the cathode.

Further, the operation is only really practicable when we use a source of electricity giving 1·1 volt on an open circuit. Thus we may be certain of never surpassing the maximum indicated, even when the resistance of the bath becomes very great, and all checking of the current is useless; with a higher voltage it is almost impossible to obtain the desired result by introducing metallic resistances into the circuit, as is often done. Neither is it necessary to trouble about the quantity of the current, which is always very low.

No. of expt.	Silver in solution. Grm.	Lead in solution. Grms.	Ag : Pb.	HNO_3. C.c.	Alcohol. C.c.	Temperature.	E.M.F. Volts.	Total volume. C.c.	Time. Hours.	Silver found.	Differences.
1.	0·0108	2·5	1 : 231	2	6	60°	1·0	130	8	0·0108	0
2.	0·0054	2·5	1 : 462	2	6	60	1·0	130	6½	0·0056	+0·0002
3.	0·0054	5	1 : 924	2	6	60	1·1	250	6½	0·0054	0
4.	0·0054	10	1 : 1850	2	6	60	1·1	350	8	0·0052	−0·0002
5.	0·0054	20	1 : 3703	2	6	60	1·1	300	7	0·0054	0
6.	0·0054	40	1 : 7407	2	6	60	1·1	500	6½	0·0052	−0·0002
7.	0·0054	100	1 : 18,518	2	6	60	1·1	500	6½	0·0066	+0·0012
8.	0·0054	100	1 : 18,518	4	6	60	1·1	500	8½	0·0054	0
9.	0·0054	100	1 : 18,518	5	6	60	1·1	500	6½	0·0052	−0·0002

NOTE.—In Experiment No. 7 we found a little lead in the metal deposited on the cathode.

The volumes of the solutions to be electrolysed being generally very considerable, we use as the cathode the platinum gauze recommended by Winckler; for the anode we prefer either a thick platinum wire bent into a helix, or a small cylinder of sheet platinum pierced with several holes, having the same height as the cathode and a diameter of 15 m.m.

Our solutions were obtained by dissolving a definite weight of pure nitrate of lead in a known volume of distilled water, and then adding a titrated solution of nitrate of silver so as to introduce the desired quantity of the latter metal. We also added a few c.c. of pure concentrated nitric acid and 6 c.c. of alcohol at 95°. The whole was poured into a Bohemian glass vessel of suitable dimensions. Care must be taken not to add too little acid, otherwise a little lead might be deposited with the silver (see Experiment No. 7). A minimum quantity of acid of 1 per cent of the total volume appears to be a suitable amount.

At the ordinary temperature the deposit of silver is badly and incompletely effected; on the other hand, all goes easily and completely if we heat the liquor to 55—60°.

Under these conditions, the nitrate of lead remains almost inert; in certain cases only, when the solution is sufficiently concentrated, or the density of the current at the anode becomes relatively strong, we obtain a slight deposit of brown peroxide.

This circumstance is a very favourable one, as it enables us to operate in the presence of as great a weight of lead as we wish.

The duration of the operation is about seven hours; it is especially necessary to prolong the experiment sufficiently when extracting the silver from a considerable quantity of liquid. In such a case it is also indispensable to stir the solution frequently so as to bring all portions of it into contact with the electrodes.

In the accompanying table will be found a summary of a certain number of our experiments.

These results show that it is possible to extract small quantities of silver quantitatively, even from concentrated solutions of nitrate of lead, and, further, the process is sensitive, for it is evident that we could operate in the presence of still larger amounts of lead than those we have used; it would suffice to increase the quantity of free acid and the volume of the solution in a corresponding manner, or, if the amount of silver obtained in a preliminary experiment is too small to be weighed with sufficient accuracy, we could place the electrodes successively in several solutions of the same materials.

For the detection of silver in commercial lead (sheet lead), we proceed in the following manner:—The metal is first melted and run into sticks to get rid of the outer layer; we then dissolve 100 grms. in pure nitric acid diluted with water. The solution is evaporated to dryness on the water bath to drive off the excess of nitric acid, and the salt is taken up with 500 c.c. of distilled water. After the addition of the nitric acid, and alcohol we electrolyse as above. The weight of silver found was 0·0042 grm., or one part in 23809.

This lead contained a small quantity of copper, but this did not interfere at all, as copper is not deposited with such a low electromotive force. We have also made certain that bismuth is not deposited in the conditions under which we operated.

A second sample gave for 100 grms. of metal 0·0012 grm. and 0·0009 grm. of silver in two experiments, or practically one part in 100,000.

With a third sample of the commercial metal we found 0·0015 grm. of silver, or one part in 75,000.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 13.

VOLUMETRIC ESTIMATION OF THE LIME AND MAGNESIA SIMULTANEOUSLY PRESENT IN SOLUTIONS OF CHLORIDE OF SODIUM (BRINES FROM SALT-MARSHES).

By ALEX. D'ANSELME.

THIS method depends upon the use of NaOH mixed with CO_3Na_2 in titrated solution.

We have observed that the salts of magnesia in a saturated solution of common salt are completely precipitated by a solution of CO_3Na_2 mixed with a sufficient quantity of NaOH in the proportion of $4CO_3Na_2$ to one of NaOH; this does not take place with CO_3Na_2 alone. This solution is titrated in the presence of tropeoline with molecular SO_4H_2; we then proceed as follows:—

1. The salts of lime and magnesia are estimated together.
2. The lime salt is estimated alone.
3. The amount of lime is deducted from the salts of lime and magnesia together, and the difference gives the amount of magnesia.

The volumetric data, given by operations 2 and 3, are transformed into grms. per litre corresponding to the salt of lime or magnesia, by multiplying the figures observed by 1·36 for sulphate of lime and by 0·95 for chloride of magnesia.

Method of Procedure.

1. *Simultaneous Titration of the Salts of Lime and Magnesia.*—Take 100 c.c. of the sample, and add 10 c.c. of the above solution; heat, filter, and titrate the filtrate, and the observed value deducted from the titration value of 10 c.c. of the solution added, will give by difference the value for the salts of lime and magnesia together.

Comparative Results obtained with a Raw Brine from a Salt-marsh.

Degrees Baumé at 15°	..	24·7	
Density at 15°	.. .. ..	1·207	
NaCl	.. ..	314·4	grms. per litre
SO_4Ca volumetrically	.. ..	2·720	,, ,,
SO_4Ca gravimetrically	..	2·723	,, ,,
$MgCl_2$ volumetrically	.. ..	0·750	,, ,,
$MgCl_2$ gravimetrically	..	0·751	,, ,,

2. *Titration of the Salt of Lime alone.*—Take 100 c.c. of the solution, and add 100 c.c. of 10 per cent chloride of ammonium, then 10 c.c. of the above mentioned titrated solution; this must not be heated for fear of completely decomposing the chloride of ammonium by means of the caustic soda. Filter, wash well, and titrate the filtrate; the difference between this value and that obtained with the lime and magnesia together will give the value of the magnesia.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 14.

NOTE ON THE USE OF A NEW DENATURISING AGENT FOR COMMERCIAL ALCOHOLS.

By M. CARI-MANTRAND.

In the year 1895, I published in the *Moniteur Scientifique* a communication on the insufficiency of the present methods of denaturising commercial alcohols. In the course of this paper I showed that by special treatment it was possible to recover from alcohol denaturised by the official method,* at least 75 per cent of an alcohol suitable for purposes of consumption. The price of treatment, with the integral recovery of the denaturising substance, can be reduced to 12 francs per hectolitre.

In publishing this method I reserved to myself the right of communicating to the Consultative Committee of Arts and Manufactures a new denaturiser of more certain efficacy than the methylene or wood-spirit officially adopted. This substance, taken from among the series of methylic derivatives, offers the advantage of not being able to be separated by the fractional distillation of the ethylic alcohol, or by the method which I had used for the revivification of denaturised alcohol, a process also applicable to the elimination of all substances suitable for denaturising, such as heavy oils from coal-tar, pyrogeneous oils, aromatic essences, &c.

Now, as the old method of denaturisation by methylene has been adhered to, in spite of its imperfections, I have abstained from mentioning my new denaturiser.

But as at the present time a commission has been appointed by the Minister of Finance to prepare a complete revision of the law on spirits and commercial alcohols, the moment appears to me to be opportune to state that in 1895 I recommended cyanide of methyl (acetonitrile) boiling at 82°, density at 15° = 0·819 as a good denaturising agent.—*Bull. Soc. Chim.*, Series 3, vol. xxix., No. 14.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month ending November 30th, 1903.

By SIR WILLIAM CROOKES, F.R.S., and PROFESSOR DEWAR, F.R.S.

To Charles Perrin, Esq., M.Inst.C.E., *Water Examiner, Metropolis Water Act*, 1871.

London, December 10th, 1903.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 203 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 1st to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 203 samples examined by us during the month, all were clear, bright, and well filtered.

The rainfall at Oxford shows a deficit during the past month. The actual amount of rain measured during November was 1·47 inches; the average fall is 2·30 inches. Thus we have a deficit of 0·83 inch, which, if deducted from the previous excess of 12·57 inches, leaves a total excess for the year of 11·74 inches, or 50·7 per cent on the thirty-five years' average.

Our bacteriological examinations of 351 samples taken during last month have given the results recorded in the following table. Besides these samples we have examined 356 others from special wells, standpipes, &c., making a total of 707 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	845
New River, filtered (mean of 61 samples) ..	25
Thames, unfiltered (mean of 25 samples)	18,390
Thames-derived water from the clear-water wells of eight Thames-derived supplies (mean of 193 samples)	43
Ditto ditto .. .. highest	572
Ditto ditto .. .. lowest	0
River Lea, unfiltered (mean of 24 samples) ..	610
River Lea, from the East London Water Company's clear-water wells (mean of 23 samples)	28

Of the 277 daily samples taken from the filter wells of the Metropolitan Water Companies, eleven samples, or 4·0 per cent, were sterile. Thirty samples, or 10·8 per cent, contained more than 100 microbes, and of these, sixteen samples contained more than 150 microbes per c.c. The thirty excess samples contained an average of 168 microbes per c.c. In October fifty-one excess samples contained an average of 186 microbes per c.c. The above figures show that there has been a considerable improvement in the bacterial character of the impounded and filtered supply during the past month, although the condition of the crude water taken from the Rivers Lea and Thames was worse than during October.

The soluble organic matter in the supply derived both from the Lea and Thames has been steadily diminishing during the course of the month. The brown colour also has become less.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

The Central.—Under this title there has just been published the first number of a new monthly magazine, edited on behalf of the Committee of the City and Guilds of London Central Technical College Old Students' Association, by Dr. E. F. Armstrong and M. Solomon. The two principal aims of the editors are, firstly, to produce a magazine which will be of interest to the Central Students, past, present, and future, and, secondly, to produce a magazine worthy of the college, and which shall serve as a permanent record of the valuable work it is doing. We congratulate the editors on the excellent literary character of the first number of their new venture. It is well printed on good paper, and has an excellent portrait of Prof. W. C. Unwin as frontispiece. The only fault we have to find is with the abominable wire-binding. Such a form of binding should never be used for any book which is intended to be read; it makes the holding of the volume troublesome and tiring, and many people will not look at a magazine or book fastened up in this style.

* Circular of June 25, 1873, No. 61; formula for denaturisation:—

Alcohol at 90°	100	litres
Methylene	15	,,
Heavy benzine (boiling-point 150—200°) .	0·5	,,
Malachite green	2	grms.

ACTION OF METALLIC MAGNESIUM UPON AQUEOUS SOLUTIONS.*

By LOUIS KAHLENBERG.

IT has long been known that metallic magnesium acts extremely slowly upon distilled water, and that it practically does not act at all upon solutions of the caustic alkalis. In 1899, Tommasi (*Bull. Soc. Chim.*, 1899, [3], xxi., 885—887) made qualitative investigations of the action of magnesium on aqueous solutions of the following salts:— KCl, NH_4Cl, $CaCl_2$, $MgCl_2$, NaCl, LiCl, $BaCl_2$, $SrCl_2$, $CuCl_2$, $CdCl_2$, $PbCl_2$, $HgCl_2$, $FeCl_3$, $CrCl_3$, $PtCl_4$, $AuCl_3$, $CuSO_4$, $ZnSO_4$, $FeSO_4$, $MnSO_4$. He found that from solutions of sodium, potassium, and lithium chloride, magnesium liberates hydrogen more rapidly than from pure water, magnesium hydroxide being formed. Solutions of the chlorides of barium, strontium, and calcium were acted upon but feebly by magnesium, but ammonium chloride solution was attacked at a lively rate. From solutions of the salts of the heavy metals mentioned above, hydrogen was liberated by magnesium, the chloride or sulphate of that metal being formed, and a basic salt or hydroxide of the heavy metal, or the latter in the metallic state, precipitated. No theoretical explanations were attempted. In the same year, G. Lemoine (*Comptes Rendus*, 1899, xxix., 291) called particular attention to the action of magnesium upon aqueous solutions of magnesium salts. He used solutions of the nitrate, chloride, sulphate, and acetate of magnesium, but worked especially with the last three salts. From aqueous solutions of these salts, magnesium liberates hydrogen rapidly and continuously. Using magnesium in form of powder, he found that about 0·4, the calculated amount of hydrogen, was liberated from a magnesium chloride solution when the powder was present in excess, the action being finally checked by the accumulation of the precipitate formed; but up to the maximum, the quantity of hydrogen disengaged was nearly proportional to the amount of magnesium added. After magnesium had acted upon the solutions of the chloride and acetate, these were found to contain but a relatively slight excess of the base. The analytical data show that the precipitates formed were very basic chloride and acetate of magnesium respectively. In the case of the magnesium sulphate the solution was much weaker after the magnesium had acted upon it, a very considerable portion of the salt having been thrown down in combination with the magnesium hydroxide in form of a basic sulphate of magnesium. Lemoine's explanation of the action of magnesium on solutions of magnesium salts is that in these solutions the salts are slightly decomposed into magnesium hydroxide and free acid. This acid acts on the metal, forming hydrogen and a basic salt which breaks up into the normal salt and hydroxide of magnesium; the latter finally drops out of solution and the reaction begins anew. In advancing this explanation it would certainly seem that Lemoine did not give due weight to the fact that the reaction of the solutions of the magnesium salts towards indicators is perfectly neutral at the outset, and that soon after introducing the magnesium it becomes alkaline and remains so, while the liberation of hydrogen continues unabated. There are thus no facts upon which to base the assumption that the salts he used are even slightly decomposed by water into free acid and magnesium hydroxide.

H. Mouraour (*Comptes Rendus*, 1900, cx., 140) again directed attention to the fact that magnesium liberates hydrogen readily, not only from solutions of its own salts, but from solutions of other salts as well. He found solutions of the carbonate, chloride, oxalate, and sulphide of ammonium strongly acted upon; but no action was observed in the case of a solution of ammonium fluoride. Sodium carbonate, acetate, and tetraborate solutions were strongly acted upon, as were also solutions of ordinary and chrome alum. On the other hand, the action was feeble on solutions of sodium phosphate, nitrite, thiosulphate, potassium ferrocyanide, and the chlorides of barium, calcium, and potassium. The work was entirely qualitative in character. Mouraour states that while Lemoine's explanation of the action may hold good in the case of solutions of chloride of magnesium, for instance, for the most of the salts last mentioned it is inadequate. In the case of the ammonium salts, Mouraour ascribes the action to the fact that solutions of these salts dissolve magnesium hydroxide. But he states that in the case of the salts of lead, copper, mercury, and cobalt, from which magnesium precipitates the heavy metals and simultaneously liberates hydrogen, we have a secondary action of the magnesium on the water of the solution. He deems it very difficult to explain the phenomena in the cases last mentioned, stating that it is not probable that salts of these heavy metals favour the solubility of magnesia. Mouraour was apparently not aware of the work of Tommasi. As a matter of fact, magnesium hydroxide is not formed at all when solutions of the heavy metals named are acted upon by magnesium; the salt of the latter metal forms and remains dissolved, the basic salt or hydroxide of the heavy metal being precipitated. In fact, the cases which Mouraour finds difficult to explain are really most readily explained, for the salts of the heavy metals are indeed slightly decomposed by water, a small quantity of free acid being liberated, as the acid reaction of such solutions clearly shows. This acid acts on the magnesium, evolving hydrogen and forming the corresponding magnesium salt, a basic salt or hydroxide of the heavy metal resulting simultaneously.

In presenting to my students the various ideas that have from time to time been entertained by scientific men regarding the nature of solutions, I have always laid considerable stress upon the view that the process of solution depends upon a mutual interaction of solvent and solute and that solutions are chemical combinations* of solvent and solute according to variable proportions. Although this view has of recent years been relegated to the background by many, it certainly has a formidable array of facts to support it; and such facts have really been accumulating more and more, though the investigations yielding them have been guided to a considerable extent by the analogy between gases and solutions. If when a substance is dissolved in water chemical combination between that substance and water takes place, the liberation of hydrogen from the solution ought to result with a different degree of readiness than from pure water. With this as the guiding idea, Mr. O. W. Brown and Dr. H. V. Black at my suggestion made some preliminary experiments in this laboratory last summer, comparing the rate with which hydrogen is evolved from various aqueous solutions by the action of magnesium upon them. In the course of these experiments (among which many of the observations of the above named French investigators were confirmed, though at the time their researches had not been looked up) it was found that hydrogen was liberated with different rapidity in the case of each solution tested, and that this rate was different from that observed when pure water was used. To my regret Messrs. Brown and Black were unable to continue these investigations, much as they were inclined to do so. It seemed to me well worth while to follow out somewhat further the work thus begun and the results obtained in investigating the subject will now be presented.

The metallic magnesium used was of Schuchardt' manufacture. It was carefully tested, and was found to be free from carbon, and from alkali and alkaline earth metals. 0·8593 grm. of the metal yielded 0·0036 grm. of the mixed

* Read at the Washington Meeting of the American Chemical Society, and at the meeting of the Wisconsin Academy of Sciences, Arts, and Letters at Madison, December 26, 1902. From the *Journal of the American Chemical Society*, xxv., No. 4.

* Compare Mendeleeff, "Principles of Chemistry," vol. i.; Pickering on Solutions; Watts' "Chemical Dictionary"; Horstmann, Graham-Otto, "Lehrbuch der Physikalischen und Theoretischen Chemie," vol. ii

TABLE I.

(Solutions contain 2 grm.-mols. per litre, except the mannite and sodium sulphate solutions, which contain 1 grm.-mol. per litre).

Solute.	2·5 hours.	23·5 hours.	47·5 hours.	53 hours.
Distilled water (alone)	0·02	0·10	1·5	1·8
Alcohol	0·10	0·40	7·6	7·8
Glycerin	0·01	0·05	0·5	0·55
Cane-sugar	0·10	0·65	1·0	1·2
Mannite	0·08	0·20	0·4	0·55
Urea	1·2	10·6	29·0	31·0
Sodium chloride	7·4	49·8	Discontinued (*a*)	
Sodium sulphate	2·4	9·9	18·0	18·8

TABLE II.

(Solutions contain 1 grm.-molecule per litre).

Solute.	25 mins.	40 mins.	50 mins.	1 hour.	1 hr. 20 min.	1 hr. 35 mins.	2 hrs. 56 mins.	4 hrs. 23 mins.
$MgCl_2$	13·0	18·5	22·0	24·8	30·5	33·8	Discontinued.	
$MgBr_2$	4·8	7·0	8·5	9·9	13·0	14·8	24·5	33·4
$MgSO_4$	5·9	9·4	11·6	13·75	18·5	21·5	36·4	50·5
$Mg(NO_3)_2$	0·2	0·35	0·4	0·45	0·6	0·65	1·2	1·6

TABLE III.

(Solutions contain 1/10 grm.-mol. per litre).

Solute.	25 mims.	35 mins.	3 hours 31 mins.	4 hours 5 mins.	5 hours 32 mins.	22 hours 34 mins.
$MgCl_2$	10·8	14·0	43·1	47·6	Discontinued.	
$MgBr_2$	1·8	2·4	7·9	8·6	10·3	25·0
$MgSO_4$	1·8	2·4	7·9	8·6	10·3	27·0
$Mg(NO_3)_2$	0·2	0·3	1·7	1·8	2·2	3·6

TABLE IV.

(Solutions contain 1/100 grm.-mol. per litre).

Solute.	17 mins.	31 mins.	45 mins.	49 mins.	2 hrs. 25 mins.	3 hrs. 37 mins.	5 hrs. 25 mins.	22 hrs. 49 mins.
$MgCl_2$	1·8	3·2	4·7	5·2	12·2	15·6	20·0	43·0
$MgBr_2$	1·4	2·0	2·6	2·8	5·8	7·1	9·6	20·9
$MgSO_4$	1·5	2·4	3·0	3·2	6·8	8·8	11·6	29·6

TABLE V.

(Solutions contain 1 grm.-mol. per litre).

Solute.	17 mins.	31 mins.	45 mins.	49 mins.
KCl	11·5	17·5	22·5	24·0
$KCl + MgCl_2$	15·0	23·0	29·4	31·4

TABLE VI.

(Solutions contain 1/10 grm.-equivalent per litre).

Solute.	2 mins.	4 mins.	6 mins.	11 mins.	16 mins.	28 mins.	33 mins.	36 mins.	46 mins.
H_2SO_4	3·2	8·0	12·0	21·0	28·0	37·6	40·4	41·8	45·6
	1 min.	3 mins.	5 mins.	7 mins.	11 mins.	14 mins.	24 mins.	29 mins.	49 mins.
HCl	3·0	8·5	14·0	19·0	27·5	31·4	39·4	43·5	48·8

(Solutions contain 1/100 grm.-equivalent per litre).

	5 mins.	10 mins.	17 mins.	20 mins.	30 mins.	40 mins.	1 hour 5 mins.	1 hr. 20 mins.	3 hrs. 37 mins.
H_2SO_4	0·4	1·2	2·0	2·5	3·6	4·6	7·0	8·4	14·3
HCl	0·4	1·2	2·0	2·5	3·6	4·7	7·0	8·0	11·8

(*a*) The word "discontinued," when used in the tables, means that the experiment was discontinued, not that the hydrogen ceased to be evolved. The experiments in these cases had to be stopped because more gas could not be held in the tube used.

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sesquioxides of iron and aluminium. Other metals were not present in the magnesium. The latter was cut into bars of square cross-section measuring 5 m.m. on an edge, and having a length of 57·5 m.m., thus presenting a surface of 1200 sq. m.m. A large number of such bars were prepared. In each liquid to be tested, such a bar was immersed, its surface being first carefully cleaned with fine emery cloth. The action of the metal upon the liquid was noted and the volume of hydrogen evolved at different times was observed. The experiments were conducted at room temperature which was nearly 20°. The ordinary distilled water of the laboratory was used. The chemicals were either of Kahlbaum's or Schuchardt's manufacture; they were tested as to their purity, special care being taken to see that they were free from traces of heavy metals, and in the case of the salts employed, that they were perfectly

neutral. Although only one series of results will be given in each case, each series was checked by at least one additional independent series. In the accompanying tables, the first column indicates the solute employed; the heading of each succeeding column indicates the time that a bar of magnesium acted upon the solution in order to liberate the volume of hydrogen given in that column (cubic centimetres.

In the case of the urea solution, ammonia as well as hydrogen was liberated. When sodium nitrate solution is treated with magnesium, only a slight amount of hydrogen is actually evolved; this is due to the fact that the salt is reduced to nitrite. From a solution of ammonium chloride containing 2 grm.-mols. per litre, over 50 c.c. of gas, consisting of hydrogen and ammonia, were liberated by one of the bars of magnesium in five minutes.

It was found that in normal potassium or sodium hydroxide solutions no measurable amount of hydrogen was evolved in twenty-four hours, the magnesium remaining perfectly bright. Solutions of magnesium nitrate when treated with magnesium yield nitrite, and finally ammonia, which accounts for the small amount of hydrogen liberated by this salt as compared with other salts of magnesium. From solutions of magnesium acetate and iodide, magnesium also evolves hydrogen rapidly. A magnesium sulphate solution was treated with a large excess of finely divided magnesium, but no reduction of the salt to sulphite took place. From a solution of crystals of $MgCl_2+6H_2O$ in glycerin of 1·27 sp. gr., magnesium evolves hydrogen; the action is much increased upon heating. Anhydrous magnesium chloride (prepared from the double magnesium ammonium chloride) dissolved in glycerin of 1·27 sp. gr. acts slowly on magnesium; this action is greatly increased upon raising the temperature. The glycerin itself acts only very slightly on magnesium even on heating. From $MgCl_2+6H_2O$ melted in its crystal water, magnesium evolves hydrogen readily. A saturated solution of $MgCl_2+6H_2O$ in ether does not attack magnesium. From a solution of 1 grm.-mol. $MgCl_2+6H_2O$ in 99·5 per cent alcohol a bar of magnesium, of the size above described, evolved 2·5 c.c. hydrogen in twenty-three hours and forty-seven minutes, while from 99·5 per cent alcohol alone a like bar of magnesium liberated 0·9 c.c. gas in twenty hours and forty-four minutes. Table I. shows that from distilled water there was evolved under like conditions only 0·1 c.c. in twenty-three and a-half hours.

The results in Table I. show that during the first twenty-three and a-half hours all the solutions except that of glycerin act more vigorously on magnesium than on water alone. Throughout the experiment the glycerin solution lags behind water. After forty-seven and a-half hours, more gas has been evolved from the water than from the solutions of glycerin, sugar, and mannite, and the same holds true after fifty-three hours. It is especially interesting to note that the alcohol solution is much more vigorous in its action on magnesium than is pure water. The urea solution is relatively vigorously attacked, though, as has been stated, ammonia is also formed in this case. Again, sodium chloride solution is much more vigorous in its action than sodium sulphate solution of equivalent strength.

Tables II., III., and IV. show that magnesium evolves hydrogen from solutions of magnesium salts at a fairly rapid rate. The solutions of the magnesium chloride are the most vigorously attacked in all cases. In the solutions containing 1 grm.-mol. per litre (Table II.) the sulphate solution is acted upon more vigorously than that of the bromide; in the solutions containing 0·1 grm.-mol. per litre (Table III.) hydrogen is evolved from the bromide and sulphate solutions at an equal rate for about five hours, within the limits of experimental error, while in the solutions containing 0·01 grm.-mol. per litre (Table IV.) hydrogen is again evolved more rapidly from the sulphate solution than from that of the bromide. In the solution of nitrate of magnesium, nitrite is formed, as mentioned above, which accounts for the fact that but little gas appears in the case of this salt. Table V. shows that the potassium chloride solution containing 1 grm.-mol. per litre acts fully as vigorously as a magnesium chloride solution of 1 grm.-mol. per litre. The double potassium-magnesium chloride acts still more strongly, as the table indicates. The observation that potassium chloride solutions act readily on magnesium agrees with that of Tommasi; Mouraour called the action feeble.

At my request, Mr. W. R. Mott measured the so-called single differences of potential between magnesium and some of the salt solutions in question. The measurements were made against the normal calomel electrode, the potential of which was taken to be - 0·56 volt. He found that at 20° C. the single potential between magnesium and sodium chloride solution (2 grm.-mols. per litre) is +1·163 volts; between magnesium and sodium hydroxide (1 grm.-mol. per litre) +1·111 volts; between magnesium and potassium hydroxide (1 grm.-mol. per litre) +1·140 volts; between magnesium and potassium hydroxide (0·1 grm.-mol. per litre) 1·105 volts; and between magnesium and magnesium sulphate (1 grm.-mol. per litre) +1·366 volts. Each result represents the average of four determinations, in which different bars of magnesium were used. In the sodium chloride solution, the electromotive force changes but slightly with the time; in the caustic alkali solutions, the electromotive force tends to fall with lapse of time; while in the magnesium sulphate solution, the electromotive force increases on standing.

The explanation of the above-described phenomena of the action of metallic magnesium upon aqueous solutions will now be considered. In the case of the saline solutions, one might feel inclined to assume that the salt acts upon the water, liberating a certain amount of free acid which attacks the magnesium, resulting in the liberation of hydrogen and the formation of a normal or basic salt or hydroxide of magnesium, according to the nature of the solution under treatment.* This would be an attempt to extend Lemoine's interpretation of the action of magnesium upon aqueous solutions of its salts to all aqueous saline solutions. As stated above, there is ground for this explanation in the case of salts of the heavy metals, whose aqueous solutions, as is well known, have acid reactions, indicating that they are indeed slightly decomposed by water, yielding free acid. But in the case of salts of Mg, Ca, Ba, Sr, K, Na, Li, there is no experimental evidence upon which to base the assumption that in their aqueous solutions there is any free acid present. Moreover, an alkaline reaction is imparted to the solutions of these salts by the magnesium soon after it has been immersed in them, and yet this alkalinity does not interfere with the evolution of hydrogen.†

There are no facts upon which to base the assumption that magnesium chloride in aqueous solution suffers greater hydrolytic decomposition (of which free hydrochloric acid is one of the products) than do the chlorides of calcium, barium and strontium for instance; and yet solutions of the last three salts are acted upon but feebly by magnesium, while from the magnesium chloride solution hydrogen is rapidly evolved. This point is illustrated still more strikingly by the fact that solutions of sodium and potassium chlorides are relatively strongly attacked by magnesium; what reasons are there to assume that these salts are decomposed more by water than those of the alkaline earth metals? And again, would it be rational to suppose that because potassium chloride solutions attack magne-

* In the language of the dissociation theory, preferred by some, it would mean that in saline aqueous solutions, from which magnesium liberates hydrogen more readily than from pure water, the salt reacts upon the water slightly, liberating some free acid, which in turn is electrolytically dissociated, yielding free hydrogen ions. The concentration of hydrogen ions in such solutions would then be greater than in pure water (which is supposed to be only slightly electrolytically dissociated), and this would account for the more vigorous action of magnesium upon saline solutions.

† According to the dissociation theory, such an alkaline solution would contain fewer hydrogen ions than pure water, and yet hydrogen is evolved faster from them than from water,

sium more readily than sodium chloride solutions, the former salt is decomposed more by water than the latter? But the difficulty of this mode of explanation becomes even greater in the case of the non-saline solutions. So, for instance, the alcoholic solution is acted upon more vigorously than pure water; clearly there is no chance for assuming free acid to be the active agent in the case of this solution.*

The idea that Mouraour advances in the case of solutions of ammonium salts, namely, that the solubility of magnesium hydroxide in them determines the liberation of hydrogen from them by action of magnesium, might possibly be applied to other solutions and so the attempt be made to generalise this explanation. In addition to the ammonium salts, there are several cases that might be considered to favour this view. So magnesium hydroxide is less soluble in solutions of sodium and potassium hydroxide than in pure water, and the fact that these solutions do not attack the metal as much as does water might be regarded as a support for the view advanced. Again, since ammonium fluoride solution is not acted upon by magnesium, and since the hydroxide and the fluoride of magnesium are insoluble in a solution of ammonium fluoride, this might be urged as another striking instance of the same kind. It would, however, be a delusion to think that the insolubility of magnesium hydroxide in these solutions is what prevents the magnesium from acting upon them. This becomes evident from the following experiment. On making magnesium amalgam (by heating magnesium and mercury together) and treating normal solutions of potassium and sodium hydroxide with the same, I found that hydrogen is very rapidly evolved, magnesium hydroxide formed, and mercury set free from the amalgam. Solution of ammonium fluoride is also violently attacked by magnesium amalgam with the concomitant liberation of hydrogen. Mere contact of magnesium and mercury in these solutions will not bring about this action; the amalgam must be used.

At a given temperature and pressure the course that a chemical reaction will take is determined (1) by the chemical affinity between the reacting substances, and (2) by the relative masses of these substances. If the system consists of a solid immersed in a liquid, the rate of action depends on the amount of surface of the solid exposed to the liquid, If the product is an insoluble one and closely envelops the surface of the solid that is being acted upon, the rate of the action will be diminished because of diminution of the surface exposed. This effect of the accumulation of the insoluble product of the reaction increases, the longer the reaction goes on, and may finally practically check the process, which is clearly shown by the results of Lemoine cited above. While there can be no doubt of this effect, nevertheless the differences in the rates of evolution of hydrogen during the times recorded above are in general too great to be accounted for solely on the basis of accumulation of the precipitate. Of this I became especially convinced by treating aqueous solutions with sodium amalgam; in these cases, where no precipitate forms, similar large differences in the rate of evolution of hydrogen occur.† Again it is well to bear in mind in this connection, that during the time of duration of the above experiments but small quantities of magnesium hydroxide or basic magnesium salts were formed; in fact, in many cases a precipitate was not at all discernible. I assured myself that from a bar of magnesium that had remained in a normal solution of sodium chloride long enough to be visibly covered with a white coating, hydrogen was nevertheless much more rapidly evolved than from a fresh bar of magnesium just placed in water.

One might further be inclined to ascribe the action of magnesium on these aqueous solutions to mere contact action, *i.e.*, to so-called catalytic action of the solute or some of its ingredients, Tommasi (*loc. cit.*) states that in the case of the potassium chloride solution we apparently have the best instance of such contact action, for here the potassium chloride remains unchanged and the magnesium hydroxide only is formed. Nevertheless even here it is not an easy matter to free the latter from "adhering chlorides" by washing. It would scarcely be helpful to dismiss the matter by saying that in these diverse solutions the rate of evolution of hydrogen is increased by the catalytic action of the solute when the hydrogen is liberated more rapidly than from water, and that the rate is diminished by the negative catalytic action of the solute, when the formation of hydrogen takes place less rapidly than from water.

All the facts above presented are very readily explained on the basis of the view of solutions which suggested this research; namely, that solutions are chemical combinations of solvent and solute according to variable proportions.* It is clear that if water is chemically bound to the substance dissolved in it, the readiness with which metallic magnesium or sodium amalgam will liberate hydrogen from different solutions will in general be different. Again, the difference of potential between magnesium and the solutions would be expected to be higher in the case of solutions that are vigorously attacked than in solutions in which the action is slight. The experimental data are in accord with this. If the chemical affinity existing between magnesium and the solution (regarded as a chemical combination of solvent with solute) is sufficient to overcome the cohesion of the magnesium, the latter is attacked; from the resulting compound hydrogen splits off, and the rest may all remain as a homogeneous liquid (*i.e.*, all may remain dissolved) or further decomposition into a precipitate, the hydroxide or basic salt, and a solution may occur, and usually does occur, after the action has progressed for a sufficient time. If no precipitate forms, the rate of change is not diminished by a decrease of the surface of metal exposed, and so the reaction is apparently aided. The more readily the dissolved products are removed from proximity of the surface of the metal by diffusion aided by mechanical stirring of some kind, the more rapidly the change progresses. Usually, as the gas is rapidly evolved, the liquid receives considerable stirring from this source. If the specific attraction called chemical affinity existing between magnesium and the solution is not sufficient at the temperature of experiment, to overcome the cohesion of the magnesium, no action will take place, as in normal potassium hydroxide solution for instance; if the affinity is barely able to overcome the cohesion, the action will go on very slowly, as in the case of water. As stated above, magnesium amalgam does act on normal potassium hydroxide solution with vigour, liberating hydrogen, forming magnesium hydroxide, and setting mercury free. The explanation of the action is similar to the one just given. Here the affinity between the solution and the amalgam is sufficient to disintegrate the latter, and magnesium hydroxide forms in spite of the fact that it is difficultly soluble. Under the conditions of the experiment, it is evidently easier to abstract magnesium from magnesium amalgam than to overcome the cohesion of pure magnesium. This is in harmony with the fact that magnesium amalgam does not form when magnesium and mercury are

* Indeed from the standpoint of the dissociation theory one would have to hold that the alcobol solution contains fewer hydrogen ions than are present in pure water, and hence action ought to be less than in the latter. Moreover from the point of view of this theory, magnesium ought to act rather less on solutions of magnessum salts, for the presence of magnesium ions would militate against the formation of more of them. And again, the difference of potential between magnesium and a magnesium sulphate solution ought to be less than between magnesium and a sodium chloride solution; the facts show that just the opposite is true.

† This most interesting problem of the action of alkali metals and their amalgams upon aqueous solutions is being studied in this laboratory by Mr. Gustav Fernekes at present. His work is already well advanced.

* The view that solutions are chemical combinations according to variable proportions, does not detract one particle from the law of definite proportions which is well established in the case of so very many compounds. Horstmann (*loc. cit.*) presents the whole matter so well that it is unnecessary to dwell further upon it here.

brought together at ordinary temperatures;* it requires a higher temperature in order that the union of the metals will take place.

The view that solutions are chemical combinations of solvent and solute may seem somewhat antiquated at the present time when purely physical conceptions of solutions are in predominance. But this older view is still held by eminent chemists and physicists, for it gives an adequate cause for the process of solution, for the thermal changes accompanying the latter, and for the fact that (exclusive of the mass) the properties of a solution are never found to be quite equal to the sum of the properties of solvent and solute. Moreover, facts known at present concerning both dilute and concentrated solutions are entirely compatible with it, and it will no doubt prove a most valuable aid in further research.

PROCEEDINGS OF SOCIETIES.

THE FARADAY SOCIETY.

Ordinary Meeting, December 8, 1903.

Prof. A. K. HUNTINGTON in the Chair.

DR. LEHFELDT gave a short *résumé* of his paper on "*The Total and Free Energy of the Lead Accumulator.*"

The most convenient form in which to express the concentration of acid in the accumulator, for the present purpose, is by the molecular function (Z) of H_2SO_4. The heat of the reaction (in equivalents),—

$$\tfrac{1}{2}Pb + \tfrac{1}{2}PbO_2 + H_2SO_4 \rightleftharpoons PbSO_4 + H_2O,$$

may then be put in the form—

$$\chi - \frac{dQ}{dZ};$$

where x is the heat of reaction between the pure materials (in absence of water) and Q is the heat of formation of the mixture $Z.H_2SO_4.(1-Z)H_2O$. Numerical values of this are calculated from the experimental data already in existence for the range $Z=0$ to $Z=0{\cdot}25$, and the results shown by a curve. The free energy can be put in a similar form. A curve is drawn for it, based on E.M.F. measurements, and the latter are compared with the vapour pressures (p) of dilute H_2SO_4 by the thermodynamic relation that takes the form—

$$\log p = \frac{F}{RT}\{\int E.dx - Ex\}$$

(F = Faraday, R = gas-constant, E = E.M.F., T = absolute temperature).

DR. OGG sent in a short note in which he tested the numbers derived from Thomsen's formula, and compared them with those derived from Pickering's experiments. The former all lie below the latter, probably because the Thomsen formula does not absolutely represent the heat of mixture of H_2SO_4 and H_2O.

DR. LOWRY made some remarks on the basis of the sulphate theory, observing that sulphating is usually looked upon as a "disease."

DR. LEHFELDT, in his reply, said that the adoption of the sulphate theory was justified by the fact that measurements of the changes of weight in the Pb, PbO_2, $PbSO_4$, and H_2SO_4 agreed tolerably closely with those deduced from the equation given in the paper. Sulphating, however, was not the same as the formation of sulphate during discharge, where only a film is allowed to form, and is immediately broken down by the current.

MR. J. A. SUTHERLAND, F.I.C., F.C.S., read a paper entitled "*Bitumen in Insulating Compositions*" (Part I.).

The author points out that little or no reliable data have been published as to the use of bitumen for electrical purposes. The chief source of bitumen is Trinidad Lake, where there is estimated to be a quantity of nine million tons, which appears to be renewed to the extent of 20,000 tons annually. Upwards of 150,000 tons are exported yearly. Bitumen is also found in Venezuela, California, and on the shores of the Dead Sea; it occurs in some limestone (asphalt) as an impregnation, about 10 to 15 per cent being present, but it does not pay to extract it from this source. Its physical and chemical properties and constitution, which are fully dealt with in the paper, prove it to be infinitely superior to gas or coal tar for insulation and durability. Care should be exercised in refining; the temperature should be regulated, or the results will be injurious both for paving and electrical purposes. It is used in cable insulation, and very extensively for joint boxes and troughs for "solid laid" cables. No specification is, however, in use, and the object of this paper is to invite discussion and the views of electrical engineers to assist the author in the completion of his experiments, and to enable him to draw up a satisfactory definition of bitumen, so that users may secure the best results from its valuable non-hygroscopic and insulating qualities.

MR. GASTER referred to Roumanian sources of asphalte. He had succeeded in freeing pitch from its carbon, which could then be used for arc carbons and electrodes, but the pitch still retained too much oxygen to be a satisfactory substitute for bitumen.

DR. STEINHART strongly supported the author in his remarks regarding the desirability of arriving at some standard tests for bitumen. Physical, as well as chemical and electrical tests were required.

MR. E. KILBURN SCOTT said that some firms declare that refined pitch is as satisfactory as bitumen. Leakage troubles, especially where cables are laid in round curves, are often caused by the creeping of the cable—which can be prevented by the use of wooden bridges—and is not at all the fault of the filling-in material.

Papers by MR. COWPER-COLES and DR. PERKIN were held over, on account of the lateness of the hour, until the next meeting.

NOTICES OF BOOKS.

Knowledge Diary and Scientific Handbook for 1904. London: *Knowledge* Office. 1903. Pp. 108.

THE fourth volume of the "Knowledge Diary" has been compiled with the same care as the preceding ones. The articles contributed to the volume are of an eminently practical nature, and will be of value for purposes of reference. They deal with "The Camera Applied to Science," "Practical Meteorology," and various astronomical subjects. The diary portion of the volume is as usual arranged for one day on each page, with a few extra sheets at the end of each month for monthly notes.

Subject List of Works on Mineral Industries and Allied Sciences in the Library of the Patent Office. London: Darling and Son, Ltd. 1903. Pp. 302.

THIS subject list is No. 13 of the Patent Office Library series, and is arranged according to the same manner and system as the preceding subject lists that have been already noticed in this column.

The present volume comprises 2559 works (243 serials, 2316 text-books, &c.), representing some 5662 volumes. The catalogue entries relating to these works number 3257, and are distributed under 418 headings and sub-headings.

* At ordinary temperatures the affinity between these metals is not able to overcome their cohesions. Compare the work of Wanklyn and Chapman on magnesium amalgam in the *Journ. Chem Soc.* [2], iv., 141.

CORRESPONDENCE.

COCOANUT OIL IN MARGARINE.

To the Editor of the Chemical News.

Sir,—It may interest some of your readers, especially those who are Public Analysts, to know that there are margarines now on the market evidently containing cocnanut oil, the fat of which has a high specific gravity, a low Valenta degree, and a refraction with the butyro-refractometer corresponding with that of genuine butter fat; hence this instrument is rendered quite useless for their detection. The following are two samples that have just come under my notice :—

Specific gravity at 100°/100° F..	911·3	909·7
Reichert (5 grms.)	4·3	4·5
Valenta turbidity test	74° C.	79° C.
Butyro-refractometer at 30° C...	50°	47·5°

—I am, &c.,

E. W. T. Jones.

Wolverhampton.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxvii., No. 21, November 23, 1903.

Colour of Aqueous Solutions of Methyl-orange, and the Changes which occur during the Estimation of Acids.—P. Vaillant.—It is known that aqueous solutions of methyl-orange, which normally are yellow, change rapidly to red when in contact with acids. The author finds that the molecular absorption of aqueous solutions of methyl-orange is independent of the concentration. A series of coefficients of absorption are given for different degrees of concentration obtained by Gouy's spectrophotometer. The numbers given show that the molecular conductivity of the solutions are relatively considerable—being more than half that of HCl, and four times that of $C_2H_4O_2$. It must be admitted that aqueous solutions of methyl-orange only contain the two ordinary elements of electrolytic solution, a complete and a dissociated molecule, and that these two elements have the same yellow colour. The change of colour under the action of acids is progressive, and tends—as the quantity of acid increases—towards a limit which is independent of the nature of the acid, but is attained more rapidly with a stronger one.

Methods of Deformation and Rupture of Irons and Soft Steels.—F. Osmond, Ch. Frémont, and G. Cartaud.—The authors determine and classify the methods of deformation of the iron in various irons and soft steels.

Influence of Gases on the Separation of Metals by Electrolysis. Separation of Nickel and Zinc.—MM. Hollard and Bertiaux.—Metals whose polarisation tensions are higher than those of hydrogen (Zn, Cd, Fe, Co, Ni, Sn, and Sb) cannot practically be separated successively by a gradual increase of the electric tension of the electrodes, even though theory indicates that each metal ought to be deposited at one particular tension, called its polarisation tension. This non-agreement between theory and practice is, however, only apparent. It is true only when the solution offers great resistance and the current is feeble for the electric tension used. This current, which precipitates one of the metals at the cathode, precipitates also the hydrogen from the solution, so that a fraction only of the current is used for the deposition of the metal—a fraction much too feeble to determine complete separation. The bath owes its great resistance chiefly to the evolution of hydrogen at the cathode and of oxygen at the anode. By suppressing one or other of these gases the author obtains a current strong enough to cause the separation of metals. The suppression of oxygen at the anode by the use of a soluble anode allows of the separation of nickel and zinc, whilst the suppression of the hydrogen at the cathode by the use of a tin or cadmium cathode allows of the separation of nickel and zinc.

Oxalacetic Acid.—L. J. Simon.—Oxalacetic acid, $CO_2H—CH_2—CO—CO_2H$, can be obtained by saponification of its ether by means of concentrated hydrochloric acid. It does not differ in its essential properties from that which Fenton, on the one hand, and Wohl, on the other, obtained by different methods.

Union of Dinaphthopyryl Salts with Phenols.—R. Fosse.—The dinaphthopyryl radicle, $CH<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>O$, can substitute its atom of hydrogen for a phenol radical, giving a body of formula $O<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CH.C_nH_{p-2}OH$. These derivatives of pyrane with phenol function can be obtained by the action of the chloride, bromide, or sulphate of dinaphthopyryl on the sodium phenols. The author investigates the reactions and properties of the series of derivatives formed.

Synthesis of Nicotine.—Amé Pictet.—The author discovers a synthesis of nicotine, starting from nicotinic acid and performing the following reactions :—Nicotinic acid is etherified, then transformed by means of ammonia into an amide, then treated with sodium hypobromite, when β-aminopyridine is formed. The mucate of this base is next prepared and submitted to dry distillation. After a series of complicated reactions, a substance is obtained identical with inactive nicotine. In order to convert this inactive substance into the two optically active modifications, right-handed tartaric acid is employed.

MISCELLANEOUS.

Royal Institution.—At the General Monthly Meeting of the Members of the Royal Institution, held on Monday, the 7th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the chair, the Chairman announced the decease, on the 30th of November, of Sir Frederick Bramwell, Bart., and the following letter from His Grace the President was read :—

"Alnwick Castle, 2nd December, 1903.

"My Dear Sir William Crookes,—It is with the utmost regret that I find an important engagement in Newcastle will unavoidably prevent my attending the Monthly Meeting of the Managers of the Royal Institution next Monday, and the subsequent General Meeting of Members. I am especially grieved because it would have been a melancholy satisfaction to have had the opportunity of expressing my deep sense of the loss the Institution has sustained in the death of our respected and valued friend, Sir Frederick Bramwell. His great talents and high professional reputation are known to all the world—the deep interest he always displayed in the work of the Royal Institution, and the conspicuous services he rendered it, cannot, I think, fail to be within the cognisance of every member. But it is only those who have taken part as his colleagues in the management, and who have had the privilege of enjoying his personal friendship, who can be fully aware of his genial kindliness, his wise counsels, and his indefatigable energy. I am glad to think that we were able to do something in his lifetime to convey to him a sense of our esteem when we added his bust to our collection. To us it is a reminder of a loss which will long be felt.—Believe me, Yours very truly,

(Signed) Northumberland."

The following Resolution, passed by the Managers, was unanimously adopted:—

Resolved, That the Managers of the Royal Institution of Great Britain desire to record their deep sense of the loss sustained by the Institution in the decease of Sir Frederick Bramwell, Bart., D.C.L., LL.D., F.R.S., M.Inst.C.E. His personality, and the signal services he rendered to the Institution by his unvarying devotion to and deep interest in its welfare and in the advancement of experimental research for twenty-seven years as Manager, Honorary Secretary, and Vice-President, will be long remembered. The Managers desire to offer Lady Bramwell and her family the expression of the most sincere sympathy with them in their bereavement.

It was also announced from the Chair that Professor L. C. Miall had been elected Fullerian Professor of Physiology,

Aqueous Solutions of Ammonia.—C. Frenzel.—The author endeavours to solve the question whether in aqueous solution the ammonia is combined with the water in an almost complete manner, forming a very feeble base, or whether the major portion exists simply in solution, a small fraction only being in combination forming a powerful base. The author has already shown (*Zeit. Electrochem.*, vol. vi., p. 477) that the conductivity of liquid NH_3 is considerably diminished by the addition of traces of water, while a subsequent addition exercises only a very feeble influence on the conductivity. The very slight tendency of trivalent nitrogen to change into pentavalent nitrogen, the thermochemical data relating to the history of ammonia, and the hydrolysis of the ammoniacal salts, are all facts in favour of the hypothesis of a feeble base. Ammonia possesses a double function; a very slightly acid one with trivalent nitrogen, and a very strongly basic function with pentavalent nitrogen ($NH_4.HO$, for example); between these two functions a well-defined equilibrium should be established in each case. For the same solution the product of the acid function and of the basic function of the ammonia remains constant, and is independent of the nature of the acid added. The formation of nitrogen in the electrolysis of solutions of ammonia is the result of a secondary action of the anodic oxygen on the solution, $4NH_3+3O_2=2N_2+6H_2O$. Even concentrated solutions only give small quantities of oxygen.—*Zeit. Anorg. Ch.*, vol. xxxii., p. 319.

MEETINGS FOR THE WEEK.

TUESDAY, 29th.
THURSDAY, 31st.
SATURDAY, Jan 2nd.
} Royal Institution, 3. (Christmas Lectures adapted to a Juvenile Audi ory). "On Extinct Animals," by Prof Ray Lankester, M.A., LL.D., F.R.S.

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Further particulars on application to the Director—

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Syllabus on application to—

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